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March 6, 2014

Richard Ho
New Jersey Remediation Branch
USEPA Region II
290 Broadway, 19th Floor
NY, NY 10007-1866

Subject: High Concentration Arsenic Area Treatability Testing Update and Supplemental Investigation

Dear Mr. Ho:

On behalf of Honeywell, CH2M HILL has prepared this treatability testing update and letter work plan for additional investigation related to the high concentration arsenic area (HCAA) within the Quanta Resources Corporation Superfund Site, Operable Unit 1 (OU1). The treatability testing for the HCAA defined within the EPA-approved Remedial Design Work Plan (RDWP; CH2M HILL 2014) was completed on January 6, 2014. While some results from this phase of treatability testing were generally successful in reducing the leachability of arsenic in site soils, some aspects of the testing have raised questions about the long-term suitability of the tested treatment mechanism. Lines of evidence suggest that groundwater within the HCAA is more reducing than was originally suspected requiring additional evaluation to harness the natural geochemistry where possible, to avoid the difficulties associated with trying to dramatically change in situ redox conditions and to avoid the potential for the re-release of arsenic as conditions shift back at some point following reagent injection.

This letter details the means and methods for collecting and analyzing additional groundwater samples at the site to further understand geochemical attributes of the HCAA and inform additional treatability evaluations. The groundwater data will be incorporated into an existing geochemical model for the site; the refined model will be used to identify additional potential reagents and preliminary dosages that would promote the formation of stable arsenic-sequestering minerals based on the existing site geochemistry. The objective of the additional modeling will be to identify the most promising reagents and rough dosages that could be further tested.

This letter work plan provides updates to the field tasks and field sampling plan (FSP) components of the work associated with the HCAA as required under the OU1 Remedial Design/Remedial Action Consent Decree (CD) for Civil Action Number 2:12-CV-7091-SRC-CLW. Data collection efforts will also be incorporated into the final design for the remedy of HCAA under the Consent Decree being developed by EPA.

Treatability Testing Update

Treatability testing for ISCF of arsenic in the HCAA as defined in the RDWP has been completed and additional field data is required to move forward with a field demonstration and pilot study. Batch testing and column studies using a ferrous sulfate treatment showed reductions of arsenic leachability within the fill material; however, tests on the native sand actually indicated an increase in arsenic leaching. It would be preferable to

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treat the entire HCAA with a single stabilization approach therefore additional evaluation of potential stabilization methods is warranted before moving into a field demonstration.

Data collected during the PDI and as part of the treatability study suggest that groundwater may be more reducing than originally suspected, and that sulfides may be present in both the fill and native sand groundwater. Sulfide minerals have been documented to sequester arsenic, and enhancing this process/mechanism in situ should be considered as an ICSF approach for the HCAA.

Field Sampling Plan

Sediment Sampling

Prior to groundwater sampling, attempts will be made to collect samples of sediments that have accumulated at the base of the well screen. The sample will be collected so that anoxic conditions are maintained, to the extent practicable. The sediment sample will be collected by placing peristaltic pump tubing on the bottom of the well and the sediment and water (presumed to be suspended to some degree in the groundwater) will be pumped out passed through a field filter to allow the accumulation of the sediment on the filter surface. Sediment will be removed from the filter, placed in a bag and shipped. During sampling, the sediment color, grain size, and odor will be noted. Additional detail on the sampling procedure is provided in the attached task specific Uniform Federal Policy – Quality Assurance Project Plan (UFP-QAPP). Sediment samples will be evaluated using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

XRD will indicate the mineral phases in the sediment which will then be used to determine which metals should be analyzed. For example, should the XRD indicate pyrite, pyrite constituents (iron and sulfur) plus arsenic will be analyzed.

SEM can show the crystal morphology of pyrite or other minerals, thereby confirming the XRD and wet chemical analysis. Electron diffraction analysis (EDX) may also be performed if deemed necessary on individual crystals while under the electron microscope, which provides data similar to XRD on a smaller scale.

The individual analyses for sediment are listed in Table 1.

Groundwater Sampling

An existing site geochemical model will be refined to further understand the in situ geochemical conditions and to identify and assess potential treatment reagents and dosages. The first step to refining the model includes field parameter measurements, and limited groundwater and in-situ well sediment sample collection and analysis. These data will provide more confidence in the current redox state of both the fill and native sand groundwater and greater resolution around some of the critical groundwater parameters, such as alkalinity, dissolved organic carbon, and sulfide. Groundwater samples for analytical testing will be collected using low-flow sampling methods in accordance the original FSP (Parsons, 2005b) and as described in the 1998 “USEPA Region II Groundwater Sampling Procedure Low Stress (Low Flow) Purging and Sampling”. Additional details are provided in Attachment A, UFP-QAPP. Groundwater samples will be collected from the eight monitoring wells within the HCAA, shown on Figure 1, samples will be analyze for the following:

- Alkalinity using field testing procedure 8023 and laboratory analysis SM2320
- Ferrous iron using field testing procedure Model IR-18C
- Sulfide using field testing procedure 8131 and laboratory analysis Method 4500-SD-D
- Presence or absence of sulfate reducing bacteria using Biological Activity Reaction Test (BART) procedure SRB-BART from HACH
- Sulfate and chloride using ion chromatography (Method E300)

- Methane using laboratory analysis RSK-175
- Ortho-phosphate using laboratory Method SM 4500-PE
- Select dissolved metals using laboratory EPA Method 6010B
- Total Petroleum Hydrocarbons (Diesel Range Organics and Gasoline Range Organics) using laboratory EPA Method 8015M
- Dissolved organic carbon using laboratory Methods E9060 and SM5510B.
- Sulfur isotope geochemistry using a laboratory ion exchange method

The individual analyses for groundwater and sediment are listed in Table 1.

Equipment Decontamination and Waste Management

Groundwater and sediment sampling equipment will be decontaminated in accordance with SOP #003 (within UFP-QAPP) and investigation-derived waste will be managed in accordance with the Waste Management Plan as detailed within the approved RDWP (CH2M HILL, 2014).

Reporting

Data collected as part of this sampling will be used to refine the existing geochemical model, which has been performed using PHREEQC. PHREEQC is a computer program written by USGS for simulating chemical reactions and transport processes in natural or contaminated water. PHREEQC will be used to further understand the treatability testing results and refine the most adequate treatment for the HCAA. The objectives include:

- Refine the understanding of the in situ geochemical conditions in the native sand and fill units. This evaluation will include, but not necessarily be restricted to, review of variables such as metal speciation, mineral saturation indices, and oxidation-reduction indicators.
- Evaluate the general geochemical effects of adding a range of potential treatment reagents and dosages to the native sand and fill units and assess the ability to facilitate long-term sequestration of arsenic within the sand and fill units.
- Identify the most promising reagents for field-scale and possible bench-scale testing to further determine injectability, effectiveness, and dosage optimization.

Once the modeling is complete, the results will be summarized in a technical memorandum detailing the proposed next steps and pilot test for the HCAA ISCF treatment.

Health and Safety

All field demonstration activities will be conducted in accordance with the current site health, safety, and environment plan, dated June 2013, and included as Appendix F of the RDWP Addendum (CH2M HILL, 2013).

Schedule

The field activities are currently scheduled for early March. Field work is anticipated to take three days. Sample analysis, data evaluation, supplemental modeling and reporting will take approximately eight weeks to complete. The results of the geochemical modeling and proposed approach for additional treatability testing or field demonstrations are anticipated to be submitted to EPA by Spring 2014.

If you have any questions in regards to the information provided herein, feel free to contact me at 267-250-7387 or Steve Coladonato, Honeywell Remediation Manager, at 302-791-6738.

Sincerely,

CH2M HILL

Stephen J. Zarlinski
Project Manager

WP-HCAA_GW Sampling
c: Steve Coladonato (Honeywell)
Erica Bergman (NJDEP)

TABLE 1

Proposed Sampling Approach

Quanta Resources Superfund Site

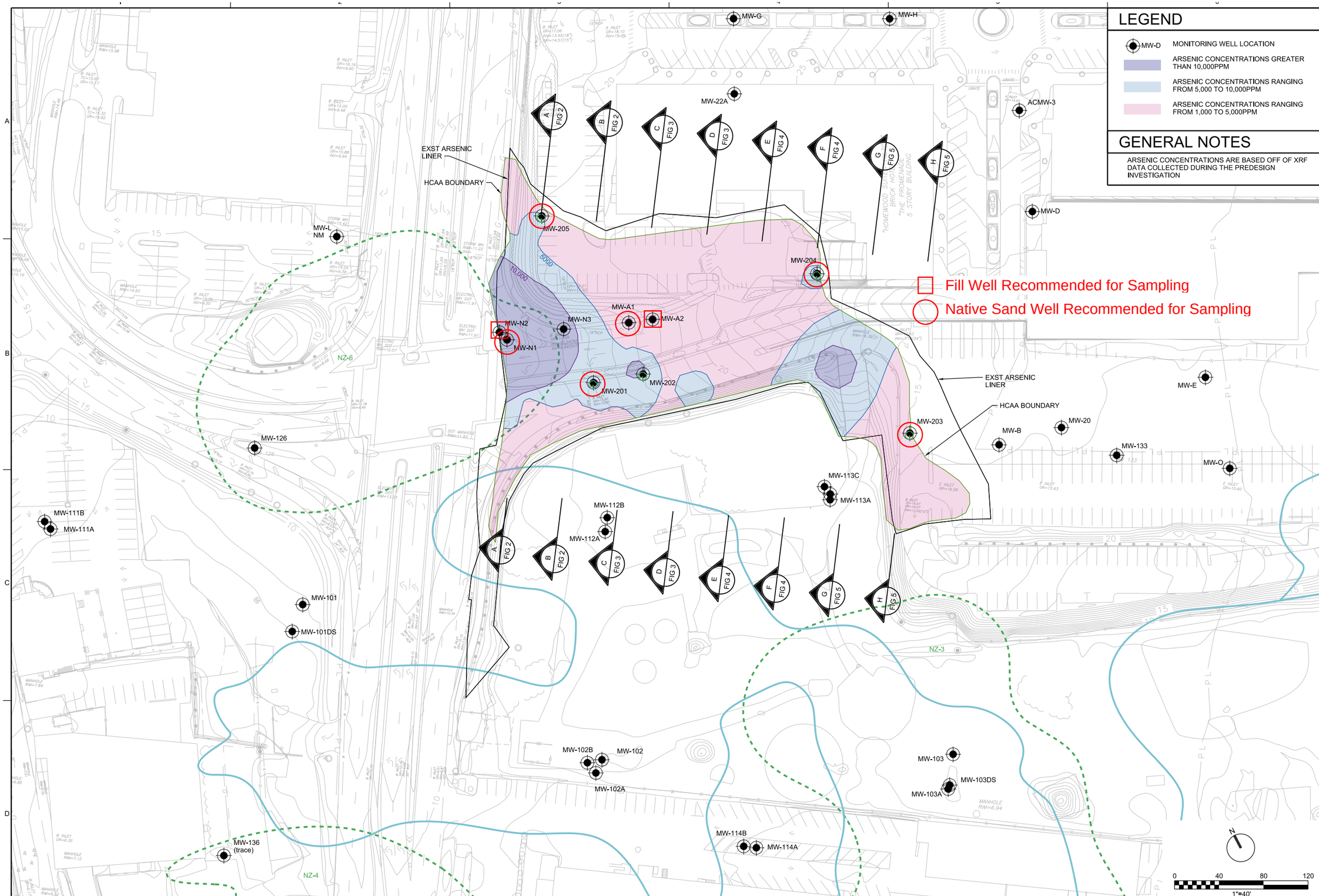
	Media:	Well Sediment			Groundwater														
		Sulfide Mineral Assessment															Organics Analysis		
	Parameter:	Total Iron, Arsenic, and Sulfur	Bulk & clay mineral fractions	Pore system and distribution of matrix and cement constituents	pH	Alkalinity		Ferrous Iron	Sulfate Reducing Bacteria (presence/ absence)	Sulfide		Sulfate	Sulfur Isotope (^{32}S /^{34}S)	Chloride	Ortho-phosphate	Select Dissolved Metals[1]	Dissolved Organic Carbon	TPH (Diesel and Gasoline Range)	Methane
	Analysis Location:	Lab	Lab	Lab	Field	Field	Lab	Field	Field	Field	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
	Method:	XRF	Quantitative XRD	SEM	pH probe	Hach 8203	SM 2320 B	Model IR-18C	HACH SRB-BART	Hach 8131	SM 4500-S2-D	E 300.1	Ion Exchange	E 300.0	SM4500-PE	E 6010B	E 9060	E 8015M	RSK 175
	Preservative:	Sealed in air-tight bag, placed on ice			none	none	none	none	none	none	zinc acetate	none	cold - rapid ship	none	none	HNO_3	H_2SO_4 or HCl	none/HCl	HCl
Well ID	Formation																		
MW-A-2	Fill	X	X	X	X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-N-2	Fill	X	X	X	X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-202	Native Sand				X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-203	Native Sand	X	X	X	X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-204	Native Sand				X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-205	Native Sand				X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-A-1	Native Sand	X	X	X	X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-N-1	Native Sand	X	X	X	X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O

Notes:

O - Field-filtered sample (includes all metals associated method 6010B and additional cations)

X - Non-field-filtered sample (included anions)

[1]Select dissolved metals include arsenic, calcium, iron, magnesium, manganese, potassium, and sodium



LEGEND

- MW-D — MONITORING WELL LOCATION
- ARSENIC CONCENTRATIONS GREATER THAN 10,000PPM
- ARSENIC CONCENTRATIONS RANGING FROM 5,000 TO 10,000PPM
- ARSENIC CONCENTRATIONS RANGING FROM 1,000 TO 5,000PPM

GENERAL NOTES

ARSENIC CONCENTRATIONS ARE BASED OFF OF XRF DATA COLLECTED DURING THE PREDESIGN INVESTIGATION

NO.	DATE	REVISION	BY	APVD

DSGN KD BLOCK | DR TB WEINSTEIN | CHK | APVD

HONEYWELL INTERNATIONAL INC.
QUANTA RESOURCES CORPORATION
SUPERFUND SITE
Client Location

CH2MHILL®

CIVIL
HCAA PLAN VIEW OF ARSENIC CONCENTRATIONS

1"=40'-0"
VERIFY SCALE
BAR IS ONE INCH ON ORIGINAL DRAWING.
0 1"

DATE
PROJ 428872
DWG
SHEET of

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FILENAME: 19-C-F215_02-28-13.dgn PLOT DATE: 2013\04\12 PLOT TIME: 12:47:52 PM

Attachment A
Task Specific UFP-QAPP

Draft

UFP-Quality Assurance Project Plan, High Concentration Arsenic Area Quanta Resources Corporation Superfund Site, OU1, Edgewater, New Jersey

Prepared for

Honeywell International Inc.

March 2014

CH2MHILL®

Document Control Number: CH2M-Quanta-HCAA-v1

Prepared using 2012 EPA guidance (http://www.epa.gov/fedfac/pdf/ufp_qapp_worksheets.pdf)

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QAPP Worksheet #35: Data Verification Procedures

QAPP Worksheet #36: Data Validation Procedures

QAPP Worksheet #37: Data Usability Assessment

References

Attachment 1 – Standard Operating Procedures

Acronyms and Abbreviations

µg	microgram
%R	percent recovery
BTU	British thermal unit
CA	corrective action
CCAL	continuing calibration
CCV	continuing calibration verification
COC	chain-of-custody
DDT	dichlorodiphenyltrichloroethane
DNAPL	dense nonaqueous phase liquid
DQI	data quality indicator
DQO	data quality objective
EB	equipment blank
ECD	electron capture detector
EOX	extractable organic halides
FD	Field Duplicate
FOP	Field Operating Procedure
FSP	Field Sampling Plan
FTL	Field Team Leader
GWCS	Groundwater Collection System
HBB	hexabromobenzene
ICAL	initial calibration
ICV	initial calibration verification
kg	kilogram
L	liter
LCS	laboratory control sample
MB	method blank
MDL	method detection limit
mg	milligram
mL	milliliter
MS/MSD	matrix spike/matrix spike duplicate
N/A	not applicable
NAPL	nonaqueous phase liquid
O&M	operations and maintenance
OU	Operable Unit
oz.	ounce(s)
PAL	Project Action Limit
PBB	hexabromobiphenyl
PCB	polychlorinated biphenyl
PDWP	Pre-Design Work Plan
PM	Project Manager
ppm	parts per million
PQO	Project Quality Objectives
QA	quality assurance
QAM	Quality Assurance Manager
QAPP	Quality Assurance Project Plan
QC	quality control
QL	quantitation limit

QM	Quality Manager
RA	remedial action
RAC	Remedial Action Contract
RDWP	Remedial Design Work Plan
RL	reporting limit
RPD	relative percent difference
RT	retention time
RTL	Review Team Leader
SM	Site Manager
SME	Subject Matter Expert
SOP	Standard Operating Procedures
SSAP	Sediment Sampling and Analysis Plan
SVOA	semivolatile organic analysis
SVOC	semivolatile organic compound
TBD	to be determined
TCLP	toxicity characteristic leaching procedure
TOC	total organic carbon
USEPA	U.S. Environmental Protection Agency
VOA	volatile organic aromatic
VOC	volatile organic compound
WAM	Work Assignment Manager

TABLE1
CROSSWALK: UFP-QAPP WORKBOOK TO 2106-G-05 QAPP

Optimized UFP-QAPP Worksheets		2106-G-05 QAPP Guidance Section	
1 & 2	Title and Approval Page	2.2.1	Title, Version, and Approval/Sign-Off
3 & 5	Project Organization and QAPP Distribution	2.2.3	Distribution List
		2.2.4	Project Organization and Schedule
4 , 7 & 8	Personnel Qualifications and Sign-off Sheet	2.2.1	Title, Version, and Approval/Sign-Off
		2.2.7	Special Training Requirements and Certification
6	Communication Pathways	2.2.4	Project Organization and Schedule
9	Project Planning Session Summary	2.2.5	Project Background, Overview, and Intended Use of Data
10	Conceptual Site Model	2.2.5	Project Background, Overview, and Intended Use of Data
11	Project/Data Quality Objectives	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
12	Measurement Performance Criteria	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
13	Secondary Data Uses and Limitations	Chapter 3	QAPP Elements for Evaluating Existing Data
14 & 16	Project Tasks & Schedule	2.2.4	Project Organization and Schedule
15	Project Action Limits and Laboratory-Specific Detection / Quantitation Limits	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
17	Sampling Design and Rationale	2.3.1	Sample Collection Procedure, Experimental Design, and Sampling Tasks
18	Sampling Locations and Methods	2.3.1	Sample Collection Procedure , Experimental Design, and Sampling Tasks
		2.3.2	Sampling Procedures and Requirements
19 & 30	Sample Containers, Preservation, and Hold Times	2.3.2	Sampling Procedures and Requirements
20	Field QC	2.3.5	Quality Control Requirements
21	Field SOPs	2.3.2	Sampling Procedures and Requirements
22	Field Equipment Calibration, Maintenance, Testing, and Inspection	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables
23	Analytical SOPs	2.3.4	Analytical Methods Requirements and Task Description
24	Analytical Instrument Calibration	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables
25	Analytical Instrument and Equipment Maintenance, Testing, and Inspection	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables

TABLE1
CROSSWALK: UFP-QAPP WORKBOOK TO 2106-G-05 QAPP

Optimized UFP-QAPP Worksheets		2106-G-05 QAPP Guidance Section	
26 & 27	Sample Handling, Custody, and Disposal	2.3.3	Sample Handling, Custody Procedures, and Documentation
28	Analytical Quality Control and Corrective Action	2.3.5	Quality Control Requirements
29	Project Documents and Records	2.2.8	Documentation and Records Requirements
31, 32 & 33	Assessments and Corrective Action	2.4	ASSESSMENTS AND DATA REVIEW (CHECK)
		2.5.5	Reports to Management
34	Data Verification and Validation Inputs	2.5.1	Data Verification and Validation Targets and Methods
35	Data Verification Procedures	2.5.1	Data Verification and Validation Targets and Methods
36	Data Validation Procedures	2.5.1	Data Verification and Validation Targets and Methods
37	Data Usability Assessment	2.5.2	Quantitative and Qualitative Evaluations of Usability
		2.5.3	Potential Limitations on Data Interpretation
		2.5.4	Reconciliation with Project Requirements

QAPP Worksheets #1 and #2: Title and Approval Page

1. Project Identifying Information
   a. Site Name/Project Name: Quanta Resources Corporation Superfund Site, Operable Unit (OU) 1
   b. Site Location/Number: Edgewater, New Jersey
   c. Contract/Work Assignment Number: NJD000606442
2. Lead Organization
   a. Lead Organization Project Manager: Steve Zarlinski/CH2M HILL

      Signature: _____ Date: _____

   b. Lead Organization Quality Manager: Kyle Block/CH2M HILL

      Signature: _____ Date: _____

3. Federal Regulatory Agency: Richard Ho/USEPA Region 2 Remedial Project Officer

   Signature: _____ Date: _____

4. State Regulatory Agency: Erica Bergman/New Jersey DEP, Project Manager

   Signature: _____ Date: _____

5. Other Stakeholders (as needed):

   Steve Coladonato/Honeywell International Inc., Site Remediation Manager

   Signature: _____ Date: _____

   Additional Personnel

   Signature: _____ Date: _____

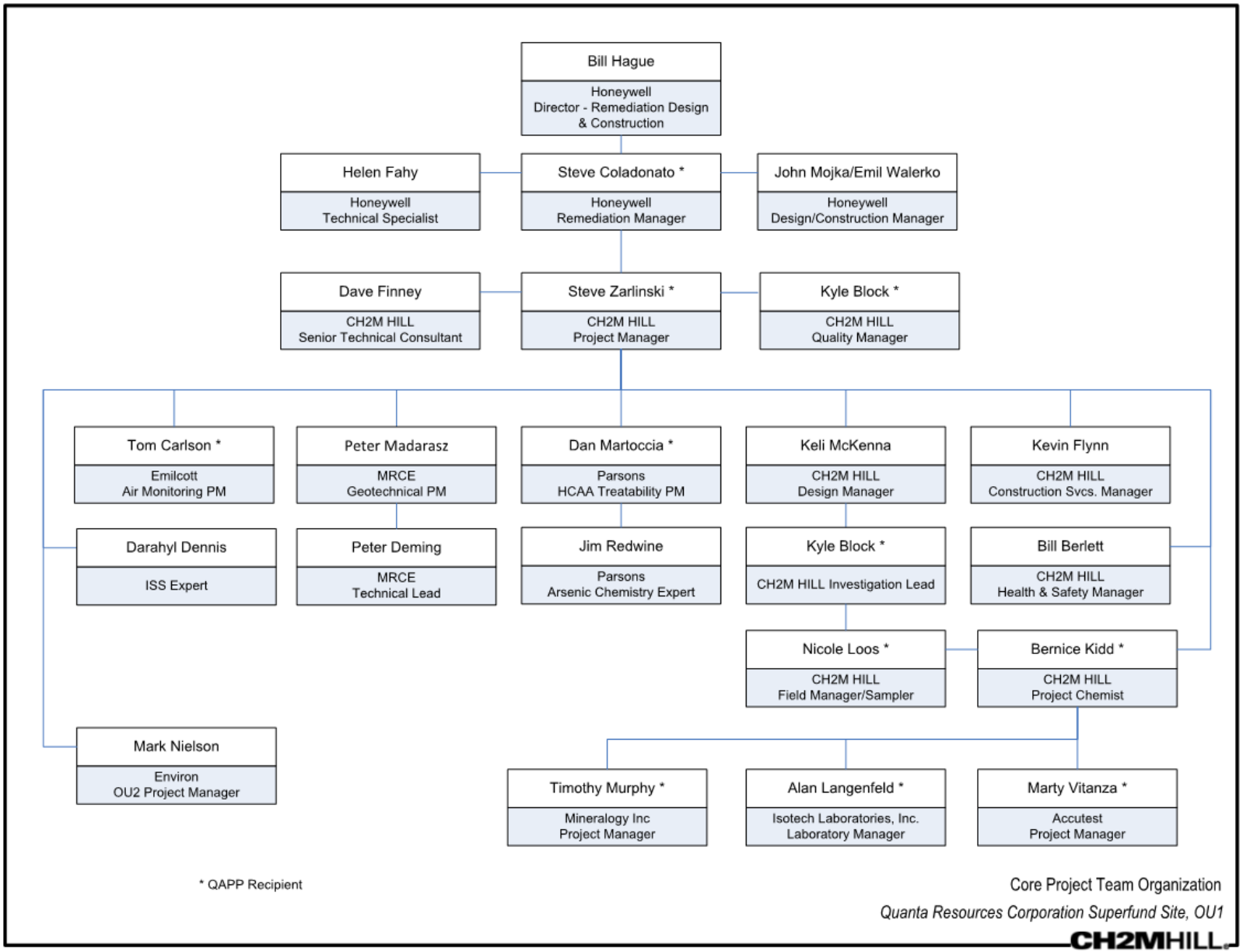
6. List plans and reports from previous investigations relevant to this project

Title	Approval Date
QAPP (Revised), Operable Unit 1, Quanta Resources OU1	October 2005
QAPP (Revised), Operable Unit 1, Quanta Resources OU1	November 2006
QAPP (Revised), Operable Unit 1, Quanta Resources OU1	July 2008
QAPP (Revised), Operable Unit 1, Quanta Resources OU1	October 2011
Quality Assurance Project Plan, Quanta Resources Corporation Superfund Site, Operable Unit 1, Edgewater, New Jersey	August 2012

Title	Approval Date
Quality Assurance Project Plan, Quanta Resources Corporation Superfund Site, Operable Unit 1, Edgewater, New Jersey	August 2013
UFP-Quality Assurance Project Plan for 2013/2014 Vapor Intrusion Sampling, Quanta Resources Corporation Superfund Site, OU1, Edgewater, New Jersey	September 2013

QAPP Worksheets #3 and #5: Project Organization and QAPP Distribution

(EPA 2106-G-05 Section 2.2.3 and 2.2.4)



QAPP Worksheets #4, #7, and #8: Personnel Qualifications and Sign-off Sheet

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date*
Organization: USEPA				
Richard Ho	Region 2 Remediation Project Manager			
Organization: NJDEP				
Erica Bergman	Remediation Project Manager			
Organization: Honeywell				
Steve Coladonato	Remediation Manager			
John Mojka/Emil Walerko	Design and Construction Manager			
Helen Fahy	Technical Specialist			
Organization: CH2M HILL				
Steve Zarlinski	CH2M HILL PM			
Kyle Block	Quality Manager			
Keli McKenna	Design Manager			
Nicole Loos	Field Manager/Field Sampler			
Bill Berlett	Health and Safety Manager			
Berney Kidd	Project Chemist			
Organization: Parsons				
Dan Martoccia	Parsons PM			

*Signatures indicate personnel have read and agree to implement this QAPP as written.

This project will require uniquely trained personnel to perform specialized field reconnaissance, sampling, onsite/offsite analysis, data review, and other project functions. All project personnel are qualified and experienced in the project tasks for which they are responsible. All field personnel will have received the required OSHA 40-hour HAZWOPER certification and the annual 8-hour refresher course, if applicable. Training records/certificates will maintained by the CH2M HILL.

In addition to the aforementioned roles, subcontractors will be utilized on this project to complete the required work. The subcontractors will include analytical laboratories and field services subcontractors. The below table provides a list of current subcontractors and their contact phone numbers. Should this list change, an updated list will be provided to the personnel listed in Section 2.3 of this QAPP.

Subcontractor	**Role**	**Contact Name**	**Telephone Number**
Accutest	Analytical Laboratory	Marty Vitanza	(732) 329-0200
Mineralogy, Inc.	Analytical Laboratory – Sediments	Timothy Murphy	(918) 744-8284
Isotech Laboratories, Inc.	Analytical Laboratory – Groundwater Sulfur Isotope Analysis	Alan Langenfeld	(217) 398-3490

QAPP Worksheet #6: Communication Pathways

Communication pathways will follow the above organizational chart (Worksheet #3). The Honeywell RPM (Steve Coladonato) and the CH2M HILL PM (Stephen Zarlinski) will be the main contact for questions or concerns. Frequent and timely team communication is important and has a direct connection to the successful delivery of the remedial design. Individual tasks are listed in Worksheets #4, #7, and #8.

Communication Driver	Organization	Name	Contact Information	Procedure (timing, pathway, documentation, etc.)
Regulatory Agency Interface	EPA Region 2	Richard Ho	212-637-4372, Ho.Richard@epamail.epa.gov	Act as liaison between PRPs and United States government agency. Review and approve necessary documents associated with sampling and results. Provide written notice to proceed and approval of reports.
Regulatory Agency Interface	New Jersey Department of Environmental Protection	Erica Bergman	609-292-7406, Erica.Bergman@dep.state.nj.us	Act as liaison between PRPs and New Jersey agencies. Review and approve necessary documents associated with sampling and results. Provide written notice to proceed and approval of reports.
All project related tasks	Honeywell International Inc.	Steve Coladonato	302-791-6738, Steven.Coladonato@Honeywell.com	Act as liaison between CH2M HILL and USEPA. Provide review of all site documents.
All project related tasks	CH2M HILL	Steve Zarlinski	810-360-2061, Steve.Zarlinski@ch2m.com	
All project related tasks	CH2M HILL	Kyle Block	617-626-7013, Kyle.block@ch2m.com	Act as liaison between sample team and greater project team. Transmit necessary information to PM on status of sampling events and analytical updates.
QAPP changes prior to field work	CH2M HILL	Kyle Block	617-626-7013, Kyle.block@ch2m.com	Review QAPP during field mobilization and prep. Initiate corrective actions or changes associated with QAPP prior to mobilization.
QAPP changes during project execution	CH2M HILL	Nicole Loos	(610) 506-1492, nloos@ch2m.com	Field Sampler to identify corrective actions. Field Sampler initiates corrective action on identified field issues immediately or as defined during review.
Field Correction Actions	CH2M HILL	Nicole Loos, Steve Zarlinski	(610) 506-1492, nloos@ch2m.com /810-360-2061, Steve.Zarlinski@ch2m.com	PM and Field Sampler to identify corrective actions. Field Sampler initiates corrective action on identified field issues immediately or as defined during review.

Communication Driver	Organization	Name	Contact Information	Procedure (timing, pathway, documentation, etc.)
Site Health and Safety Issues	CH2M HILL	Nicole Loos	(610) 506-1492, nloos@ch2m.com	Conduct Daily Health and Safety Meetings and make decisions regarding health and safety issues. Communicate with PM as appropriate.
Analytical Actions/ Reporting of Data and Release of Data, Facilitate Data Management, Sample Receipt	CH2M HILL	Berney Kidd	530-229-3203, Bernice.Kidd@CH2M.com	Provide electronic data, sample ID, locations and analysis. Transmit sample tracking information. Receive and review data packages before data is used. Initiate data validation of subcontractor laboratory data.
HCAA Treatability Tasks	Parsons	Dan Martoccia	732-537-3557, Daniel.Martoccia@parsons.com	Communicate to PM as appropriate. Work to develop appropriate approach and data evaluation techniques to further refine HCAA remedy.
Analytical Actions, Laboratory specific actions	Accutest	Kristin Beebe	732-329-0200, kristinb@accutest.com	Communicate to PM as appropriate. Document situation and effect in a data quality report prepared as part of final report.

QAPP Worksheet #9: Project Planning Session Summary

Date of planning session: January 10, 2014

Location: Conference Call

Purpose: Treatability Testing Update and Discuss Path Forward

Participants:

Name	Organization	Title/Role	Phone/Email
Steve Coladonato	Honeywell	Remediation Manager	302-791-6738, Steven.Coladonato@Honeywell.com
Steve Zarlinski	CH2M HILL	Project Manager	810-360-2061, Steve.Zarlinski@ch2m.com
Dean Williamson	CH2M HILL	HCAA Technical Lead	352-384-7204 x57204, Dean.williamson@ch2m.com
Dave Finney	CH2M HILL	Senior Technical Consultant	617-626-7024, david.finney@ch2m.com
Kyle Block	CH2M HILL	Quality Manager	617-626-7013, Kyle.block@ch2m.com
Dan Martoccia	Parsons	HCAA Treatability PM	732-537-3557, Daniel.Martoccia@parsons.com
Jim Redwine	Parsons	Arsenic Chemistry Expert	201-240-3464, James.Redwine@parsons.com
Richard Carbonaro	Mutch Associates	Geochemical Lead	201-669-4171, rcarbonaro@mutchassociates.com

Agenda

1.) Next Steps
   a. Field test and sample collection
   b. Refine geochemical model
   c. Develop approaches for application and field testing
   d. Identify additional data needs prior to field testing
2.) Review of Critical Items
   a. Obtain access with City Place to sample wells
   b. Short work plan for Item 2(a) for submittal
   c. Schedule

Action Summary	Notes	Responsible Party
Review analytical list and confirm that no additional requirements are needed to move into field demonstration	Work with Parsons and Mutch associates to develop an all-encompassing list. After this event, the next step should be a pilot test.	CH2M HILL with review from greater party
Prepare a brief work plan for submittal to EPA	Include a UFP-QAPP and short cover letter	CH2M HILL with review from greater party

Action Summary	Notes	Responsible Party
Send email to City Place updating them on the sampling plan and proposed schedule	Honeywell to provide email	Honeywell
Schedule sampling event for mid-February	Sampling event will wait until after the Super Bowl to occur	CH2M HILL
Move forward with procurement of laboratories	Specialized analysis will be done by Isotech and Mineralogy Inc.	CH2M HILL

QAPP Worksheet #10: Conceptual Site Model

This QAPP addresses sampling and analysis associated with field demonstrations for in situ solidification and in situ chemical fixation, and waste characterization. Other field activities will be addressed under separated QAPPs submitted in conjunction with relevant work plans. The following subsections present the conceptual site model for OU1.

Site Description

The Site is located at the intersection of River Road and Gorge Road in Edgewater, New Jersey. A vacant lot referred to as the Quanta property, portions of River Road and Gorge Road, and properties and portions of properties surrounding the Quanta property comprise the upland portion of the Site, or OU1. The area of OU1 is approximately 24 acres. The Site is adjacent to the Hudson River. Figure 1 depicts the properties constituting OU1.

The Quanta property contains the following:

- Exposed former tank and building foundations
- Remnants of a former oil-water separator
- A wooden bulkhead along the shoreline
- Remains of wooden docks

The property is generally flat and at a lower elevation than River Road to the west and the City Place property to the north. The Quanta, 115 River Road, and i.Park properties are all at a similar elevation, one corresponding to the land surface during industrial use (prior to 1982). River Road and City Place are located at higher elevations due to more recent placement of fill material.

Site History

The brief site history below was provided within the Record of Decision (ROD).

The Quanta site is located at River Road and the intersection of Gorge Road, Edgewater, New Jersey. At the center of the site is a 5.5-acre vacant lot, referred to as the Quanta property, surrounded by a number of developed and undeveloped parcels, portions of which are also considered part of the site. Sections of River and Gorge Roads have been constructed on top of the site. The land portion of the site is approximately 24 acres. The site also includes an area of sediment contamination in the Hudson River. The extent of the Hudson River sediments affected by the site will be determined as part of an ongoing Operable Unit 2 (OU2) Remedial Investigation and Feasibility Study (RI/FS) that is separate from this response action.

The site is characterized by contamination from a variety of industries that operated there from at least the 1870s to 1981. These industries included coal tar processing, chemical manufacturing, and waste oil storage. The 5.5-acre Quanta property is a remnant of an industrial coal tar facility that once covered approximately 15 acres.

Geology

At the upland portion of the Site, the overburden stratigraphy listed below is generally observed (in order encountered from ground surface):

Stratigraphic Unit	Description
Fill material	Up to 35 feet of fill material consisting of a mixture of gravel, sand, and silt with brick, wood, concrete fragments, coal, cinders, and slag.
Peat/clayey peat	Up to 25 feet of organic peat or meadow mat with varying amounts of clay, fine sand, and silt. The peat/clayey peat deposits are discontinuous and have been observed primarily in borings completed near River Road, Block 93, and the former Lever Brothers property.
Soft organic silt	Up to 68 feet of soft gray-to-black organic silt containing wood, roots, and shell fragments. This unit is also included in the estuarine and salt marsh deposits. The soft organic silt is typically present only within 100 feet of the shoreline throughout the entire study area and represents former river sediments that were buried during shoreline filling. It pinches out to the west and against the bedrock high to the northwest on the former Celotex property. Moving east to west, the organic silts become the main layer within the Hudson River Basin, dipping downward extending to nearly the bedrock with a thin layer of till between the silts and bedrock.
Shallow native sand	Up to 21.5 feet of fine to medium/coarse sand with varying amounts of gravel and fines. In the central portions of the Quanta property and the northern portion of the former Lever Brothers property where the peat/clayey peat and soft organic silt are absent, the shallow native sand resides directly beneath the fill unit. South of the high bedrock elevations within the former Celotex property, native sands along the shoreline dip down, eventually pinching to an end along the shoreline of the Hudson River Basin and giving way to the soft organic silts.
Silty clay (confining unit)	Up to 35 feet of continuous silty clay with varying amounts of fine sand. The silty clay represents a lake-bottom unit that underlies the estuarine and salt marsh deposits. The silty clay serves as a confining unit and an aquitard between both the overlying native sand and fill units and the underlying deep sand deposits. It is found across most of the site with an undulating surface that dips eastward in close proximity to the existing shoreline and pinches out towards the north against a bedrock high at the former Celotex property. On the southern portion, the silty clay along the shoreline dips down in a manner similar to what is observed with the native sands, eventually pinching to an end along the shoreline of the Hudson River Basin and giving way to the soft organic silts.
Deep sand	Ranging up to approximately 32 feet of fine to coarse sand, sand with varying amounts of silt and clay, and silt and clay with varying amounts of sand. The deep sand represents a lacustrine fan unit that lies beneath the confining silty clay unit. Like the overlying silty clay confining unit, the deep sand dips eastward under the Hudson River and pinches out towards the north against the bedrock high present on the former Celotex property and to the west against the rising Palisades ridge. On the southern portion of the Site, the deep sands follow the bedrock surface and extend farther from the shoreline below the “estuarine and salt-marsh deposits” into the Hudson River Basin.
Till	Up to 12 feet of a very dense, low-permeability, reddish-brown to reddish-yellow silty sand and sand with gravel, cobbles, and boulders. Along the shoreline to the south of PZ-6D, and to a lesser extent to the north Moving from east to west into the Hudson River basin, the till deposits slope downward dramatically giving way to a thickening of the organic silt deposits.
Bedrock	The Stockton Formation composes the underlying bedrock formation at the site and is found at depths ranging from 8.5 feet (at the bedrock high in the south-central portion of the former Celotex property) to 86 feet below ground surface (bgs). Its appearance in core samples collected during the RI consisted of variably consolidated alternating sandstone and siltstone lenses with a variety of colors, including, red, white, pink, brown-gray, and brown-yellow. Towards the east and southeast bedrock dips dramatically forming the Hudson River channel.

Three distinct hydrostratigraphic units exist at the Site above the bedrock surface. The shallowest unit consists of an unconfined, surficial water-bearing zone extending from the water table—approximately 4 feet below ground

surface (bgs)—to approximately 15 to 20 feet bgs. This unit is underlain by a silty clay aquitard approximately 10 to 20 feet thick. Last, a confined water-bearing "deep sand" unit between 5 and 20 feet thick exists between the aquitard (confining unit) and the surface of the bedrock (Stockton Formation). The shallow saturated zone and deep sand units are not hydraulically connected.

Shallow groundwater flowing eastward toward the Hudson River is largely diverted to flow north and south once it reaches the shoreline, as a result of the presence of a wooden bulkhead. However, much of the groundwater above the clay confining unit flows beneath the bulkhead in the organic silt and shallow sand. Groundwater discharges to surface water through the river sediments in areas of upwelling north of and adjacent to the wooden bulkhead and to a lesser degree offshore south of the bulkhead.

Source Areas

Soil and groundwater at OU1 contain constituents from industries that operated on various portions of the Site from at least the 1870s to 1981, including coal tar processing, chemical manufacturing, and waste oil storage. A substantial amount of data and information was collected and assessed during the OU1 RI and various supplemental investigations and has achieved the objective of completing a comprehensive site characterization of the Site. The RI and various supplemental investigations included the following:

- Characterization of OU1 sources
- Determination of the nature and extent of contamination
- Evaluation of fate and transport of constituents of interest (COIs)
- Assessment of potential risks to human health and the environment

Soils at OU1 have been found to contain source material in the form of principal threat and low-level threat waste. Principal threat wastes are considered source materials, that is, materials that include or contain hazardous substances, pollutants or contaminants that act as a reservoir for migration of contamination to groundwater, surface water, or as a source for direct exposure. Principal threat wastes are those source materials considered to be highly toxic or highly mobile that generally cannot be reliably contained or would present a significant risk to human health or the environment should exposure occur.

NAPL

The location, nature, and extent of the NAPL at OU1 have been comprehensively delineated through the RI process for the purposes of remedial design and implementation. NAPL is found throughout the Site and is made up of aromatic volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs). Most of the SVOCs are polycyclic aromatic hydrocarbons (PAHs). Coal tar materials found at the Site range from low-viscosity liquids to solid tar. NAPL at the Site is identified as either free-phase or residual NAPL. Free-phase NAPL is able to collect in monitoring wells, whereas residual NAPL is present in quantities insufficient to allow mobility. Most of the free-phase NAPL at the Site is denser than water and is present in six discrete areas (NAPL zones [NZs] 1 through 6), shown in Figure 1. These NZs were defined on the basis of one or more of following factors:

- Thickness of visually observed NAPL as well as TarGOST response indicating NAPL
- Lateral and vertical separation between areas where visual observations and TarGOST results indicated significant thicknesses of NAPL
- Observation of free-phase (i.e., mobile) NAPL in monitoring wells

All principal threat NAPL at the Site (i.e., the portion of the NAPL for which active remediation is required per the ROD) is present within the boundaries of these six zones (Figure 1). Exposure through direct contact, ingestion, or inhalation is plausible for NZ-1 and NZ-2, and the potential is likely that future use of the Site could result in exposure if appropriate remedial actions are not implemented. Direct exposure to NAPL in NZ-3, NZ-4, or NZ-6 is unlikely, even under a construction scenario, given their depth (generally deeper than 10 feet below ground surface). Without additional remedial effort, there is the potential for the migration of free-phase NAPL to

sediment and surface water in the Hudson River from NZ-2 and NZ-5. As indicated in the ROD, release of free-phase NAPL from NZ-1, NZ-3, NZ-4, and NZ-6 to sediments is not plausible.

Outside the defined NAPL zones and throughout the Site, NAPL is present as residual NAPL or thin, discontinuous pockets of free-phase NAPL that have not been found to be contiguous with the defined NAPL zones. These areas contain constituents exceeding soil remediation values but are not identified as source areas, and therefore they "can generally be managed in place with engineering controls (capping) and proper land-use restrictions." (ROD)

High-Concentration Arsenic Area

The HCAA lies beneath a cover and fill material, and a portion is located beneath an active access ramp to the City Place development. The extent of the HCAA is defined as soil concentrations of arsenic greater than 1,000 milligrams per kilogram (mg/kg). The 1,000 mg/kg boundary (i.e., the HCAA) as depicted was developed using historical data collected during the investigation, remediation, design, and development of the City Place property, and new data collected during the RI and supplemental investigations. The cover placed during construction of the City Place development extends beyond the delineated 1,000 mg/kg boundary along the edge of River Road on the Quanta property. The extent of the HCAA and the extent of the cover are depicted in Figure 1.

Arsenic Areas

Eight separate sources of soluble arsenic to groundwater and of other inorganic constituents in groundwater were identified as principal threat waste within the lateral extent of OU1 but outside the HCAA. Each arsenic area has elevated soil concentrations that have a potential direct-contact risk to human health defined as greater than 390 mg/kg for arsenic contamination in the shallow, unsaturated soils (approximately the first 4 feet of surface soil) and 1,000 mg/kg for deeper soils. The ROD refers to these areas as "shallow arsenic hotspots," although these areas may contain residual NAPL or overlap areas delineated as NAPL zones (Figure 1). One of these arsenic areas (referred to as AA-3), located on the i.Park property, was excavated in December 2010 by i.Park Edgewater, LLC, with oversight by CH2M HILL. The remaining seven arsenic source areas and the HCAA are depicted in Figure 1.

Site-wide Soil

Outside the areas defined as NAPL zones, residual NAPL, discontinuous pockets of free-phase NAPL, and site-related constituents are found in saturated and unsaturated soil. The primary site COCs driving the remediation are VOCs, SVOCs, and metals, particularly arsenic and lead. Remedial evaluations and design are being based on a subset of representative constituents:

- VOCs: benzene, ethylbenzene, toluene, and xylenes
- SVOCs: naphthalene and benzo(a)pyrene
- Arsenic
- Lead

Some of the remaining constituents detected less frequently above the soil remediation goals will be addressed in source areas through the remedial actions for the source areas. Outside the source areas, capping and institutional controls will meet the remedial action objectives for these other constituents by preventing direct contact.

Site-wide Groundwater

Similar Site-related constituents were detected in groundwater throughout the site. As noted in the ROD, "groundwater contamination above screening criteria, with similar constituents, has been identified from remedial investigations of all neighboring properties"; therefore, a complete delineation of the extent of groundwater impacts from the Site is not possible. EPA concluded that the factors listed below along with "the presence of off-site sources and regional characteristics…would undermine a successful restoration within OU1."

Type of Factor	Characteristics Limiting Groundwater Restoration Potential
Contaminant	Widespread presence of NAPL (primarily as DNAPL), and recalcitrant DNAPL-related constituents
	Long history of industrial use and associated releases at and outside of the site
	Volume and depth of contaminated media
	Presence of arsenic in soil and groundwater, and the collocation of arsenic and DNAPL
Hydrogeologic	Complex geology consisting of interbedded and undulating layers of sands, silts and clays with discontinuous peat deposits
	Heterogeneous soil conditions and the presence of low permeability materials such as silts and clays
Site setting	Highly urbanized environment with significant surficial and subsurface infrastructure

DNAPL, dense non-aqueous-phase liquid.

A waiver of groundwater Applicable or Relevant and Appropriate Requirements (ARARs) within the OU1 boundary was granted by EPA on the basis of technical impracticability from an engineering perspective, and Remedial Action Objectives (RAOs) were developed to prevent unacceptable exposure and limit offsite migration. The complete evaluation of groundwater restoration potential is documented in the technical impracticability evaluation (CH2M HILL, 2010).

Remedial Action Objectives

The ROD established RAOs for principal threat waste, soil, and groundwater. Remedial action objectives for principal threat wastes and other media at the Site are as follows:

Material	Remedial Action Objectives
Principal threat waste	Remove, treat, or contain principal threat waste, to the extent practicable.
	Prevent exposure to NAPL and arsenic source material that poses an unacceptable human health risk.
	Prevent current or potential future migration of free-phase NAPL to the Hudson River or to areas that would result in direct contact exposure.
	Mitigate free-phase NAPL that poses a potential source of vapor intrusion and resulting inhalation exposure within existing or potential future structures.
	Mitigate NAPL and arsenic principal threats as sources of groundwater contamination, to the extent practicable.
Soil	Prevent or minimize potential human exposure through direct contact, ingestion, dust inhalation, or vapor intrusion that presents unacceptable risk from exposure to contaminated soil attributable to the site.
	Prevent or minimize potential erosional transport off site or to the Hudson River of contaminated soils at concentrations posing unacceptable risk.
Groundwater	Prevent or minimize potential exposure by contact, ingestion, or inhalation/vapor intrusion that presents unacceptable risk from exposure to contaminated groundwater attributable to the site.
	Prevent migration and preferential flow of site contaminants in groundwater to sediments and surface water of the Hudson River at levels posing an unacceptable risk to human health or ecological receptors.

Selected Remedial Action

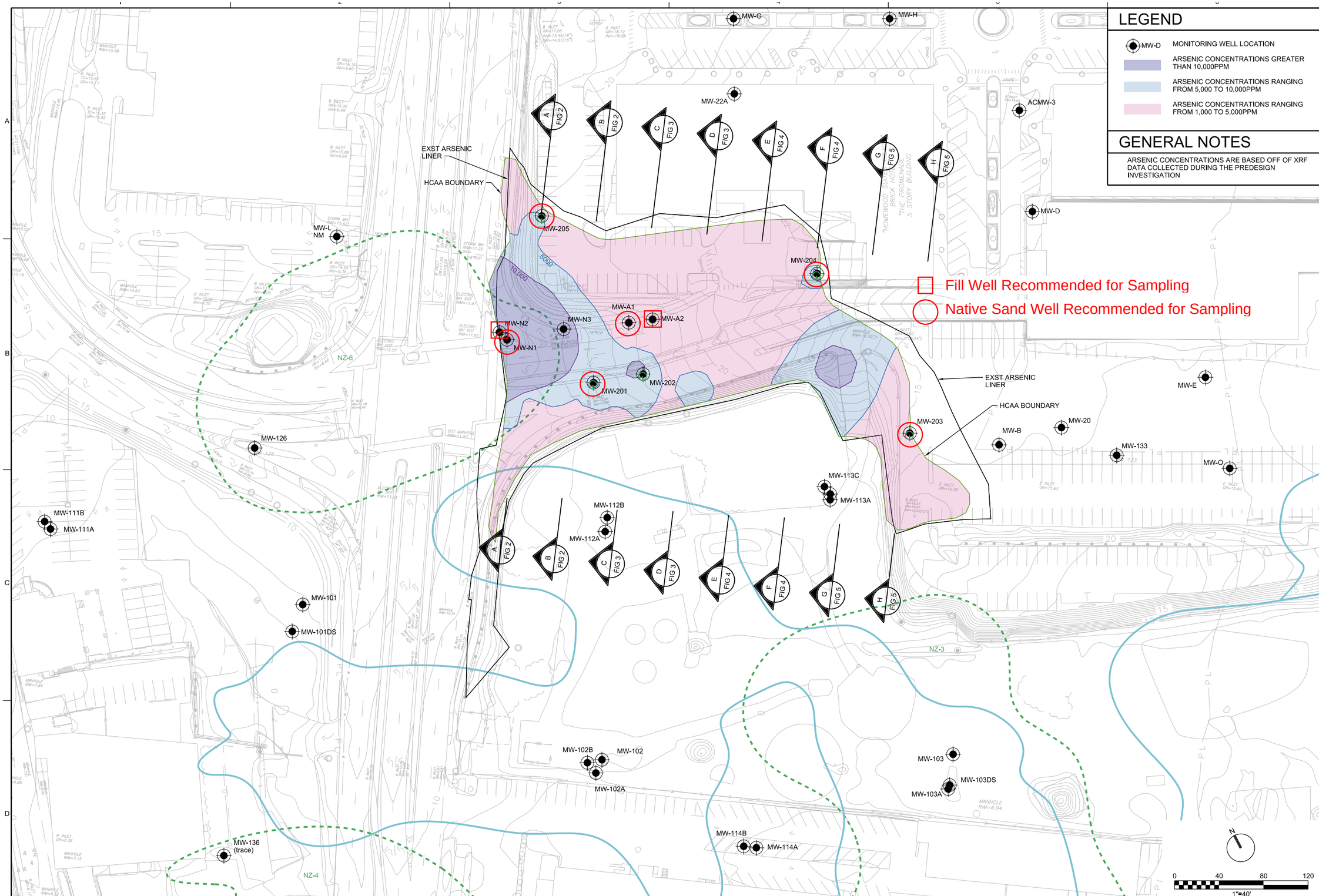
The Selected Remedy described within the ROD involves the solidification/stabilization of NAPL and arsenic source areas, capping and institutional controls, coupled with the installation of a groundwater containment remedy, a subaqueous reactive barrier in the Hudson River to mitigate contaminated groundwater releases. The components of the Selected Remedy include:

- On-site solidification/stabilization of an estimated 150,000 cubic yards of contaminated soil containing arsenic and NAPL, primarily by in-situ solidification/stabilization (ISS).
- Remaining deep NAPL will be collected utilizing recovery wells or recovery trenches and NAPL collected and disposed of offsite.
- Installation of a vapor mitigation system and basement sealing at 115 River Road; construction of a temporary barrier wall at 115 River Road along the shoreline to isolate untreated free phase NAPL from the Hudson River and sediments.
- Capping of contaminated soils remaining on site at concentrations greater than the Remediation Goals for residential direct contact with a multilayer cap as approved by EPA.
- Installation of a subaqueous reactive barrier (SRB) in Hudson River sediments, coordinated with a future OU2 remedy.
- Operation and maintenance for the active components of the remedy, such as the Deep NAPL collection system and vapor intrusion systems, monitoring of the site over the long term to assure the protectiveness of the Remedy, and institutional controls; implementation of a long-term sampling and analysis program to monitor the contamination at the site in order to assess groundwater migration, and the effectiveness of the remedy over time.

Uncertainties and Data Gap

During the recent treatability testing, some of the results indicated that the HCAA may be more of a reducing environment than initial field characterization data has suggested. Lower than expected soil pHs were measured in the laboratory prior to treatment than were measured in the field at the time of sample collection. This suggests that some geochemical changes occurred from the field to the lab, one possibility being the oxidation of reactive sulfides. Furthermore, arsenic speciation, dissolved iron, and sulfide data in groundwater collected during the PDI all suggest at least an iron reducing environment and perhaps even a sulfate reducing environment is present within the HCAA.

Work to identify reagent types and dosages performed to date has focused mechanisms for treating arsenic that are most suitable in more oxidizing groundwaters. The data collected as part of the treatability testing, in addition to that collected during the HCAA characterization component of the Pre-design investigation suggest that further investigation is warranted to better understand the redox state of the HCAA groundwater before proceeding with the ISCF design. This work is detailed in Worksheet #11, #17, and #18.



LEGEND

- MW-D — MONITORING WELL LOCATION
- ARSENIC CONCENTRATIONS GREATER THAN 10,000PPM
- ARSENIC CONCENTRATIONS RANGING FROM 5,000 TO 10,000PPM
- ARSENIC CONCENTRATIONS RANGING FROM 1,000 TO 5,000PPM

GENERAL NOTES

ARSENIC CONCENTRATIONS ARE BASED OFF OF XRF DATA COLLECTED DURING THE PREDESIGN INVESTIGATION

NO.	DATE	REVISION	BY	APVD

DSGN KD BLOCK | DR TB WEINSTEIN | CHK | APVD

HONEYWELL INTERNATIONAL INC.
QUANTA RESOURCES CORPORATION
SUPERFUND SITE
Client Location

CH2MHILL®

CIVIL
HCAA PLAN VIEW OF ARSENIC CONCENTRATIONS

1"=40'-0"
VERIFY SCALE
BAR IS ONE INCH ON ORIGINAL DRAWING.
0 1"

DATE
PROJ 428872
DWG
SHEET of

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QAPP Worksheet #11: Project/Data Quality Objectives

This QAPP addresses additional data required to refine treatability testing for the HCAA. In order to minimize uncertainties in the treatability study and define a path forward, additional work plan components are required which include the collection of groundwater samples at the site to further understand the geochemical attributes of the HCAA. Data will be used by CH2M HILL and Honeywell to refine the appropriate remedy associated with the HCAA. Data for this event will be provided to USEPA and NJDEP for their review as part of the design process associated with the ROD.

These data will be incorporated into a geochemical model. The model will be used as a baseline for model-based evaluations of potential treatments. The model will be used to identify additional potential reagents and preliminary dosages for creating stable forms of arsenic-sequestering minerals that are congruent with the natural geochemistry at the site. The objective of the additional modeling will be to identify the most promising reagents that could be further tested.

The project-specific detections limits for each sampled media are specified on Worksheet #15 for all parameters and media which are being analyzed. Data will meet the DQO's that have been specified for the site per Worksheet #12, 18, and 28.

The sampling design and rationale, including the location and reason for each individual sample is included within Worksheet #17 and #18 of this UFP QAPP. Worksheets #19, 20, 24-28, and 30 specify additional analysis design requirements.

Data collected as part of this scope will be archived in accordance with Worksheet #29. Data from the subcontracted laboratories will be received in electronic format and validated accordingly by CH2M HILL. Hard copies of the field data including the field logs will be archived in the project files.

QAPP Worksheet #12: Measurement Performance Criteria

As part of the remedial design, environmental samples will be collected on several matrices. Environmental samples will be required to meet selected measurement performance criteria (MPC) as indicated in the below tables. The quality of the data to be collected for this project will be verified through appropriate MPCs established for both sampling procedures and analytical methods. These MPCs should be satisfied in order to support defensible decisions and provide sufficient data for ultimately completing the implementation of the remedial action.

The MPCs should relate to data quality indicators (DQIs), consisting of precision, accuracy, representativeness, comparability, completeness, and sensitivity, commonly referred to as precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS) parameters. The DQIs are defined as follows:

Precision

Precision is a measure of reproducibility of measurements. It can be defined as the degree of mutual agreement among individual measurements obtained under similar conditions. Total precision is a function of the variability associated with both sampling and analysis. Precision will be evaluated as the relative percent difference (RPD) between duplicate sample results.

Accuracy

Accuracy refers to the degree of agreement between an observed value (such as sample results) and an accepted reference value. A measurement is considered accurate when the reported value agrees with the true value or known concentration of the spike or standard within acceptable limits.

Representativeness

Representativeness describes the extent to which a sampling design adequately reflects the environmental conditions of a site. Representativeness is determined by appropriate program design, with consideration of elements such as proper well locations, drilling and installation procedures, operations process locations, sampling locations and analytical procedures. Factors that can affect representativeness include site homogeneity, sample homogeneity at a single point, and available information around which the sampling program is designed. Using multiple methods to measure an analyte can also result in non-representativeness of sample data.

Comparability

Comparability addresses the degree to which different methods or data agree or can be represented as similar. Comparability is achieved by using standard methods for sampling and analysis, reporting data in standard units, normalizing results to standard conditions, and using standard and comprehensive reporting formats.

Completeness

Completeness is a measure of the amount of valid data collected using a measurement system. Completeness is expressed as a percentage of the number of measurements that are specified in this Work Plan.

Sensitivity

Sensitivity is the ability of a method or instrument to detect the target analytes at the level of interest. Sensitivity can be measured by calculating the percent recovery of the analytes at the quantitation limit, which is the minimum concentration of an analyte that can be routinely identified and quantified above the method detection limit by a laboratory.

Matrix: Water

Analytical group or method: TPH-GRO/DRO, SW8015B

Concentration level: All

Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample or Measurement Performance Activity	QC Sample Assesses Error for Sampling (S), Analytical (A), or Both (S&A)
Precision	RPD, reference WS#28	FD, MS/MSD, LCS/LCSD, Laboratory duplicate	S&A
Accuracy/Bias	Percent recovery, reference WS#28	LCS, MS, surrogates, internal standards, calibration	A
Completeness	≥95% for water matrices	Percent completeness, measure of the amount of valid data obtained compared with the amount that was expected to be obtained	S&A
Representativeness	Contamination of sample or extract with a target analyte(s)	MB, TB, EB	S&A
Comparability	Qualitative measure for field sampling and analytical procedures	Industry standard methods, QAPP compliance	S&A
Sensitivity	Verification of accurate assessment of data at the RL where the RL meets project objectives	In control calibrations, MBs, current and valid RL for the matrix/method.	A

Matrix: Water

Analytical group or method: Metals - SW6010C, SW6020

Concentration level: All

Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample or Measurement Performance Activity	QC Sample Assesses Error for Sampling (S), Analytical (A), or Both (S&A)
Precision	RPD, reference WS#28	FD, MS/MSD, LCS/LCSD, laboratory duplicate, serial dilutions	S&A
Accuracy/Bias	Percent recovery, reference WS#28	LCS, MS, post-digestion spikes, internal standards, calibration, interference check standards	A
Completeness	≥95% for water matrices	Percent completeness, measure of the amount of valid data obtained compared with the amount that was expected to be obtained	S&A
Representativeness	Contamination of sample or extract with a target analyte(s)	MB, EB, CB	S&A
Comparability	Qualitative measure for field sampling and analytical procedures	Industry standard methods, QAPP compliance	S&A
Sensitivity	Verification of accurate assessment of data at the RL where the RL meets project objectives	In control calibrations, MBs, current and valid RL for the matrix/method.	A

Matrix: Water

Analytical group or method: General chemistry, SM2320B, SM4500-Fe, SM4500-S2D, E300.0, SM4500-PE, RSK175, SW9060

Concentration level: Medium

Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample or Measurement Performance Activity	QC Sample Assesses Error for Sampling (S), Analytical (A), or Both (S&A)
Precision	RPD, reference WS#28	FD, MS/MSD, LCS/LCSD, laboratory duplicate	S&A
Accuracy/Bias	Percent recovery, reference WS#28	LCS, MS, calibration	A
Completeness	≥95% for water matrices	Percent completeness, measure of the amount of valid data obtained compared with the amount that was expected to be obtained	S&A
Representativeness	Contamination of sample or extract with a target analyte(s)	MB, EB, CB	S&A
Comparability	Qualitative measure for field sampling and analytical procedures	Industry standard methods, QAPP compliance	S&A
Sensitivity	Verification of accurate assessment of data at the RL where the RL meets project objectives	In control calibrations, MBs, current and valid RL for the matrix/method.	A

Matrix: Water

Analytical group or method: Sulfur-Isotope Analysis by Ion Exchange*

Concentration level: NA

Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample or Measurement Performance Activity	QC Sample Assesses Error for Sampling (S), Analytical (A), or Both (S&A)
Precision	RPD (laboratory derived)	laboratory duplicate	S&A
Accuracy/Bias	Percent recovery (laboratory derived)	check standard	A
Completeness	NA	NA	NA
Representativeness	NA	NA	NA
Comparability	NA	NA	NA
Sensitivity	NA	NA	NA

* the data from this specialty analysis will not be validated

Matrix: Sediment

Analytical group or method: Total Iron, Arsenic and Sulfur by XRF, Bulk and Clay Mineral Fractions by XRD, Pore System and Distribution of Matrix and Cement Constituents by SEM*

Concentration level: NA

Data Quality Indicator (DQI)	Measurement Performance Criteria	QC Sample or Measurement Performance Activity	QC Sample Assesses Error for Sampling (S), Analytical (A), or Both (S&A)
Precision	RPD (laboratory derived)	laboratory duplicate	S&A
Accuracy/Bias	Percent recovery (laboratory derived)	check standard if applicable	A
Completeness	NA	NA	NA
Representativeness	NA	NA	NA
Comparability	NA	NA	NA
Sensitivity	NA	NA	NA

* the data from these specialty analyses will not be validated.

QAPP Worksheet #13: Secondary Data Criteria and Limitations

Secondary data refer to historical data previously collected for the sites. The source(s) of the data, date of collection, planned uses, and limitations of the secondary data for each site are summarized in the following table.

Data Type	Source	Data Uses Relative to Current Project	Factors Affecting the Reliability of Data and Limitations on Data Use
GW, SW, SS, SB, Sediment, NAPL	Various, historical	Historical data to be used as needed based on limitations	The data is treated as screening-level qualitative measurements since full analytical QC data was not received with the data nor was there conclusive indication that full review was conducted.
Soil, GW,	CH2M HILL, OU1 RI	To help identify potential source areas and to help plan sampling locations	No limitation
Soil, GW, SW, Air, NAPL	CH2M HILL, OU1 SI	To help identify potential source areas and to help plan sampling locations	No limitation
Sediment	CH2M HILL, OU2 sediment study	To help identify potential source areas and to help plan sampling locations	No limitation
Air	CH2M HILL, vapor intrusion events	To help identify potential source areas and to help plan sampling locations	No limitation
Soil, GW, SW, PW	CH2M HILL, 2008–2009 SRI	To help identify potential source areas and to help plan sampling locations	No limitation
Soil	CH2M HILL, 2008–2009 soil sampling	To help identify potential source areas and to help plan sampling locations	No limitation
Sediment	CH2M HILL, 2008 OU2 BERA	To help identify potential source areas and to help plan sampling locations	No limitation
Soil, NAPL	CH2M HILL, 2010 soil sampling	To help identify potential source areas and to help plan sampling locations	No limitation
Soil, NAPL	CH2M HILL, 2011 soil sampling	To help identify potential source areas and to help plan sampling locations	No limitation
GW, Soil, Air	CH2M HILL, 2012 PDI	To help identify potential source areas and to help plan sampling locations	No limitation

Notes:
BERA— baseline ecological risk assessments
GW—groundwater
PCB—polychlorinated biphenyls
PDI—Pre-Design Investigation
RI— Remediation Investigation
SI—Supplemental Investigation
SRI—Supplemental Remediation Investigation
SVOC—semi-volatile organic compounds
TPH—total petroleum hydrocarbons
VOC—volatile organic compounds

QAPP Worksheets #14 and #16: Project Tasks and Schedule

The work scope involves the following tasks:

Activity	Responsible Party	Planned Start Date	Planned Completion Date	Deliverables	Deliverable Due Date
Work Plan Submittal	CH2M HILL	January 10, 2014	January 31, 2014	HCAA Supplemental Work Plan	January 31, 2014
Procurement of Laboratory	Honeywell/CH2M HILL	January 10, 2014	February 10, 2014	Not Applicable	Not Applicable
Mobilization for sampling	CH2M HILL	March 3, 2014	March 7, 2014	Field notes	March 21, 2014
Sampling Event	CH2M HILL	March 3, 2014	March 7, 2014	Field notes	March 21, 2014
Laboratory Results Obtained	Accutest, Isotech Laboratories, Mineralogy Inc.	March 8, 2014	End of March	Report of Analyses/Data package	End of March
Submit Report to USEPA	Honeywell/CH2M HILL	Middle of April	Spring 2014	Draft Evaluation Report	Spring 2014

QAPP Worksheet #15: Project Action Limits and Laboratory-Specific Detection/Quantitation Limits

The following tables contain the list of target compounds or contaminants of concern (COCs) that will be evaluated for this project. Due to the nature of the project, no project action limits (PAL) or project quantitation limits (PQL) have been specified or are required, with the exception of air monitoring.

Matrix: Water

Analytical methods: SW8015B, SW6010C, SW6020, SM2320B, SW4500-Fe, SM4500-S2D, E300.0, SM4500-PE, SW9060, RSK175, Ion Exchange

Concentration level (if applicable): All

Analyte	Laboratory-specific Quantitation Limit (mg/L)	Laboratory-specific Detection Limit (mg/L)
Arsenic	0.00083	0.001
Arsenic (III)	0.00016	0.0005
Arsenic (V)	0.00016	0.0005
Inorganic Arsenic	0.00016	0.0005
Calcium	0.2	5
Iron	0.05	0.1
Magnesium	0.1	5
Manganese	0.002	0.015
Potassium	0.5	10
Sodium	0.1	10
TPH-DRO (C10-C28)	0.053	0.1
TPH-GRO (C6-C10)	0.038	0.2
Dissolved Organic Carbon	0.33	1
Methane	0.03	0.11
Alkalinity	1.4	5
Ferrous Iron	0.028	0.2
Sulfide	0.217	2
Sulfate	0.034	10
Chloride	0.006	2
Orthophosphate	0.009	0.05
Sulfur Isotopes	NA	NA

Matrix: Sediment

Analytical methods: Total Iron, Arsenic and Sulfur by XRF, Bulk and Clay Mineral Fractions by XRD, Pore System and Distribution of Matrix and Cement Constituents by SEM*

Concentration level (if applicable): All

Analyte	Laboratory-specific Quantitation Limit	Laboratory-specific Detection Limit
Iron	NA	NA
Arsenic	NA	NA
Sulfur	NA	NA
Bulk and Clay Mineral Fractions	NA	NA
Pore System and Distribution of Matrix and Cement Constituents	NA	NA

QAPP Worksheet #17: Sampling Design and Rationale

Sampling design and rationale were developed to evaluate groundwater within both the fill units and the sand units which have been determined to be the two treatment areas as part of the in situ chemical fixation (ISCF) work. The wells were picked to encompass both the fill and native sand units and at various locations throughout the HCAA to understand the natural geochemistry across the site. All available monitoring points within the HCAA were chosen to to maximize the coverage across this area. Sample locations and methods are specified in Table 17-1 and shown in Figure 1.

Data collected during the PDI and as part of the treatability study suggest that groundwater may be more reducing than originally suspected, and that sulfides may be present in both the fill and native sand groundwater. Sulfide minerals have been documented to sequester arsenic, and enhancing this process/mechanism in situ should be considered as an ICSF approach for the HCAA.

Sampling

Sediment Sampling

Prior to groundwater sampling, attempts will be made to collect samples of sediments that have accumulated at the base of the well screen. The sample will be collected so that anoxic conditions are maintained, to the extent practicable. The sediment sample will be collected by placing peristaltic pump tubing on the bottom of the well and the sediment and water (presumed to be suspended to some degree in the groundwater) will be pumped out passed through a field filter to allow the accumulation of the sediment on the filter surface. Sediment will be removed from the filter, placed in a bag and shipped. During sampling, the sediment color, grain size, and odor will be noted. Sediment samples will be evaluated using X-ray diffraction (XRD) and scanning electron microscopy (SEM).

XRD will indicate the mineral phases in the sediment which will then be used to determine which metals should be analyzed. For example, should the XRD indicate pyrite, then the pyrite constituents (iron and sulfur) plus arsenic will be analyzed.

SEM can show the crystal morphology of pyrite or other minerals, thereby confirming the XRD and wet chemical analysis. Electron diffraction analysis (EDX) may also be performed if deemed necessary on individual crystals while under the electron microscope, which provides data similar to XRD on a smaller scale.

The sediment field and specialty analyses data will not be validated; information for these methods is not included Worksheets 12, 19/30, 23-25, 28, 34-37.

Groundwater Sampling

An existing site geochemical model will be refined to further understand the in situ geochemical conditions and to identify and assess potential treatment reagents and dosages. The first step to refining the model includes field parameter measurements, and limited groundwater and in-situ well sediment sample collection and analysis. These data will provide more confidence in the current redox state of both the fill and native sand groundwater and greater resolution around some of the critical groundwater parameters, such as alkalinity, dissolved organic carbon, and sulfide. Groundwater samples for analytical testing will be collected using low-flow sampling methods in accordance the original FSP (Parsons, 2005b) and as described in the 1998 “USEPA Region II Groundwater Sampling Procedure Low Stress (Low Flow) Purging and Sampling”. Groundwater samples will be collected from the eight monitoring wells within the HCAA and samples will be analyze for the following:

- Alkalinity using field testing procedure 8023 and laboratory analysis SM2320
- Ferrous iron using field testing procedure Model IR-18C
- Sulfide using field testing procedure 8131 and laboratory analysis Method 4500-SD-D
- Presence or absence of sulfate reducing bacteria using Biological Activity Reaction Test (BART) procedure SRB-BART from HACH
- Sulfate and chloride using ion chromatography (Method E300)

- Methane using laboratory analysis RSK-175
- Ortho-phosphate using laboratory Method SM 4500-PE
- Select dissolved metals using laboratory EPA Method 6010B
- Total Petroleum Hydrocarbons (Diesel Range Organics and Gasoline Range Organics) using laboratory EPA Method 8015M
- Dissolved organic carbon using laboratory Methods E9060 and SM5310B.
- Sulfur isotope geochemistry using a laboratory ion exchange method

The groundwater field, sulfur isotope and sediment analyses data will not be validated.

TABLE 17-1

Proposed Sampling Approach

Quanta Resources Superfund Site

	Media:	Well Sediment[1]			Groundwater														
		Sulfide Mineral Assessment															Organics Analysis		
	Parameter:	Total Iron, Arsenic, and Sulfur	Bulk & clay mineral fractions	Pore system and distribution of matrix and cement constituents	pH	Presence/ Absence of Sulfate Reducing Bacteria	Alkalinity		Ferrous Iron	Sulfide		Sulfate	Sulfur Isotope (^{32}S /^{34}S)[1]	Chloride	Ortho-phosphate	Select Dissolved Metals[2]	Dissolved Organic Carbon	TPH (Diesel and Gasoline Range)	Methane
	Analysis Location:	Lab	Lab	Lab	Field	Field	Field	Lab	Field	Field	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
	Method:	XRF	Quantitative XRD	SEM	pH probe	Hach SRB-BART	Hach 8203	SM 2320 B	Hach Model IR-18C	Hach 8131	SM 4500-S2-D	E 300.1	Ion Exchange	E 300.0	SM4500-PE	E 6010B	E 9060	E 8015M	RSK 175
	Preservative:	cold - rapid ship			none	none	none	none	none	none	zinc acetate	none	cold - rapid ship	none	none	HNO_3	H_2SO_4 or HCl	none/HCl	HCl
Well ID	Formation																		
MW-A-2	Fill	X	X	X	X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-N-2	Fill	X	X	X	X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-202	Native Sand				X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-203	Native Sand	X	X	X	X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-204	Native Sand				X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-205	Native Sand				X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-A-1	Native Sand	X	X	X	X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
MW-N-1	Native Sand	X	X	X	X	X	X	X	X	X O	X	X	X	X	O	O	O	O	O
Field/Equipment Blank	Not Applicable							X			X	X		X	O	O	O	O	O
Trip Blank	Not Applicable																	X	

Notes:

O - Field-filtered sample (includes all metals associated method 6010B and additional cations)

X - Non-field-filtered sample (included anions)

[1] The data for this method will not be validated; information for these methods is not included Worksheets 12, 19/30, 23-25, 28, 34-37.

[2]Select dissolved metals include arsenic, calcium, iron, magnesium, manganese, potassium, and sodium

QAPP Worksheet #18: Sampling Locations and Methods

Sampling locations and methods are outlined in the following subsections.

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/Analytical Group	Sampling SOP	Comments
Sed-A-2-MMYY	Sediment	Bottom of Well	Fill Well	As per Worksheet #17	SOP#001	Decon sampling equipment as per SOP #002
Sed-N-2-MMYY	Sediment	Bottom of Well	Fill Well	As per Worksheet #17	SOP#001	Decon sampling equipment as per SOP #002
Sed -203-MMYY	Sediment	Bottom of Well	Native Sand Well	As per Worksheet #17	SOP#001	Decon sampling equipment as per SOP #002
Sed -A-1-MMYY	Sediment	Bottom of Well	Native Sand Well	As per Worksheet #17	SOP#001	Decon sampling equipment as per SOP #002
Sed -N-1-MMYY	Sediment	Bottom of Well	Native Sand Well	As per Worksheet #17	SOP#001	Decon sampling equipment as per SOP #002
MW-A-2-MMYY	Groundwater	Not Applicable	Fill Well	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-N-2-MMYY	Groundwater	Not Applicable	Fill Well	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-202-MMYY	Groundwater	Not Applicable	Native Sand Well	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-203-MMYY	Groundwater	Not Applicable	Native Sand Well	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-204-MMYY	Groundwater	Not Applicable	Native Sand Well	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-205-MMYY	Groundwater	Not Applicable	Native Sand Well	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-A-1-MMYY	Groundwater	Not Applicable	Native Sand Well	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-N-1-MMYY	Groundwater	Not Applicable	Native Sand Well	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-N-1-Dup	Groundwater	Not Applicable	Quality Control	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-205-MS	Groundwater	Not Applicable	Quality Control	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
MW-205-MSD	Groundwater	Not Applicable	Quality Control	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
FB-MMYY	Blank	Not Applicable	Field Blank	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002
EB-MMYY	Blank	Not Applicable	Equipment Blank	As per Worksheet #17	GW Sampling SOP	Decon sampling equipment as per SOP #002

The "MMYY" listed in the Sample IDs will be replaced with the appropriate month and year nomenclature based on the sampling date. Actual amount of QC samples (Equipment Blank, Duplicates, and MS/MSD) will be based on total amount of samples collected in accordance with Worksheet #20

QAPP Worksheets #19 and #30: Sample Containers, Preservation, and Hold Times

The sampling objectives for analysis by an offsite laboratory are described below. The project specific target analytes and required methods are defined in the below table along with the appropriate bottleware to be used for each analysis.

Laboratory (name, sample receipt address, POC, e-mail, and phone numbers): Accutest Laboratories New Jersey, Inc., 2235 US Highway 130, Dayton, NJ 08810, POC: Kristin Beebe, 732-329-0200, Kristinb@accutest.com

List any required accreditations/certifications: Laboratory has current NELAC and/or New Jersey certification.

Back-up Laboratory: None

Sample delivery method: Courier pickup

Analytical Group	Matrix	Method/SOP	Containers (Number, Size, and Type per Sample)	Preservation Requirements	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
TPH-GRO	Water	SW8015B/SOP EGCGRO8015C-03	Three 40 mL glass vial	HCl, pH<2, 4°C	NA	14 days	21-day
TPH-DRO	Water	SW8015B/SOP EGCDRO8015C-03	1-L amber glass	4°C	7 days	40 days	21-day
Metals	Water	SW6010C/ SOP EMA227 SW6020/ SOP EMA226-07	500 ml Polyethylene	HNO_3, pH<2, 4°C		180 days (28 days for mercury)	21-day
Methane	Water	RSK175/SOP EAT004-08	Three 40 mL glass vial	HCl, pH<2, 4°C	NA	14 days	21-day
DOC	Water	SW9060/SOP EGN234-14	250 ml Glass	H_2SO_4, pH<2, Cool 4°C after field filtration	NA	28 days	21-day
Alkalinity	Water	SM2320B/SOP EGN037-10	500 ml Polyethylene	4°C	NA	14 days	21-day
Ferrous Iron	Water	SM4500-FE/SOP EGN243-08	250 ml Polyethylene	4°C	NA	24 hours	21-day
Sulfate and Chloride	Water	E300.0/SOP EGN281-11	500 ml Polyethylene	4°C	NA	28 days	21-day
Orthophosphate	Water	SM4500-PE/SOP EGN310-03	250 ml Polyethylene	4°C	NA	48 hours	21-day
Sulfide	Water	SM4500-S2D/SOP EGN118-09	500 ml Polyethylene	NaOH plus 2mls of zinc acetate, pH>9, 4°C	NA	7 days	21-day

Analytical Group	Matrix	Method/SOP	Containers (Number, Size, and Type per Sample)	Preservation Requirements	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Arsenic Speciation As(III) & As(V)	Water	IC-ICP-MS	125-mL HDPE	EDTA, Cool 4°C, keep dark	NA	14 days	21-day

Laboratory (name, sample receipt address, POC, e-mail, and phone numbers): Isotech Laboratories, Inc.,1308 Parkland Ct, Champaign, IL 61821 POC: Alan Langenfeld, 217-398-3490, Langenfeld@isotechlabs.com

List any required accreditations/certifications: Laboratory has specialized certifications/

Back-up Laboratory: None

Sample delivery method: Fed-Ex

Analytical Group	Matrix	Method/SOP	Containers (Number, Size, and Type per Sample)	Preservation Requirements	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Specialized Lab Specific Method	Water	Sulfur Isotope Analysis*	1-Liter Polyethylene	4°C	NA	NA	21-day

* no laboratory SOP exists for this specialty analysis

Laboratory (name, sample receipt address, POC, e-mail, and phone numbers): Mineralogy, Inc.., 3321 E. 27th St., Tulsa, OK 74114, POC: Timothy Murphy, 918-744-8284, tmurphy@mineralogy-inc.com

List any required accreditations/certifications: Laboratory has specialized certifications/

Back-up Laboratory: None

Sample delivery method: Fed-Ex

Analytical Group	Matrix	Method/SOP	Containers (Number, Size, and Type per Sample)	Preservation Requirements	Preparation Holding Time	Analytical Holding Time	Data Package Turnaround
Specialized Lab Specific Method	Sediment	XRD, SEM, XRF, EXD*	1-Liter Polyethylene or Three 40 mL glass vial	4°C	NA	NA	21-day

* no laboratory SOP exists for this specialty analysis

QAPP Worksheet #20: Field QC Summary

Quality control samples will be collected to monitor accuracy, precision, and the presence of field contamination for analytical methods to be performed in the offsite laboratory. The frequency of collection of the quality control samples is outlined below.

Matrix	Analytical Group[1]	Analysis	Field Samples	Field Duplicates	Matrix Spikes	Matrix Spike Duplicates	Field Blanks	Equipment Blanks	Trip Blanks	Total No. of Samples Analyzed
Soils	Sediment	As per Worksheet #18	5	0	0	0	0	0	0	5
Liquid	Groundwater	As per Worksheet #18	8	1	1	1	1	1	1	13

[1] The sediment and groundwater field and specialty analyses data will not be validated; information for these methods is not included Worksheet 12, 19/30, 23-25, 28, 34-37.

- **Trip Blanks** - A trip blank will be prepared before the laboratory sends the sample containers. The trip blank will consist of a 40-ml volatile organic analytic vial containing distilled, deionized water, which accompanies the other aqueous sample bottles into the field and back to the laboratory. A trip blank will be included with each shipment of water samples for volatiles analysis. The trip blank will be analyzed for the same volatile organic compounds as the samples to detect any contamination from sampling and transport, and internal laboratory procedures.
- **Equipment Blanks** - Equipment blanks will be taken at a frequency of one per decontamination event, maximum of one per day sampling equipment type, minimum of one per week. An equipment blank is used to assess the effectiveness of the decontamination procedures for sampling equipment. It is a sample of deionized, distilled water provided by the laboratory, which has passed through a decontaminated bailer or other sampling apparatus. It is usually collected as a last step in the decontamination procedure, before taking an aqueous sample. The equipment blank may be analyzed for all of the parameters of interest. An equipment blank is not needed if clean disposable sampling equipment is utilized.
- **Field Blank**—A blank used to provide information about contaminants that may be introduced during sample collection, storage, and transport; also a clean sample exposed to sampling conditions, transported to the laboratory, and treated as an environmental sample..
- **Duplicates** will consist of:
  - Field Duplicate—To assess the representativeness of the sampling methods, field duplicates will be collected at a minimum frequency of one per 10 environmental samples per matrix.
  - Matrix Spike/Matrix Spike Duplicate—MS/MSD samples will be taken at a frequency of one pair per 20 field samples. These samples are used to assess the effect of the sample matrix on the recovery of target analytes.

QAPP Worksheet #21: Field SOPs

The following Field SOPs will be used for the tests conducted above. Actual SOPs are included as Attachment 1 of this UFP-QAPP.

SOP#	Title, Revision, Date, and URL (if Available)	Originating Organization	SOP Option or Equipment Type (if SOP Provides Different Options)	Modified for Project? Y/N	Comments
GW Sampling SOP	Groundwater Sampling Procedure – Low Stress (Low Flow) Purging and Sampling	U.S. Environmental Protection Agency – Region 2	Applies to all low-flow sampling procedures	No	
001	Monitoring Well Sediment Sampling , 1/20/2014	CH2M HILL	Peristaltic Pump	Yes	
002	Equipment Decontamination, 7/16/2012	CH2M HILL	Applies to all non-disposable equipment used for sampling	No	
DOC316.53.01166	Alkalinity, Phenolphthalein and Total Alkalinity, 2012	HACH Company	Applies to all groundwater samples	No	
DOC316.53.01326	Bacteria, Sulfate-reducing, semi-quantitative, July 2013	HACH Company	Applies to all groundwater samples	No	
26672-88	Iron, Ferrous, Test Kit, 5/1997	HACH Company	Applies to all groundwater samples	No	
DOC316.53.01136	Sulfide, USEPA Methylene Blue Method, 04/2013	HACH Company	DR890 Equipment, See below	No	
Method 8131	Sulfide, Methylene Blue Method, USEPA accepted for reporting wastewater analysis	HACH Company	DR890 Equipment	No	

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

Field Equipment	Activity	SOP Reference	Title or Position of Responsible Person	Frequency	Acceptance Criteria	Corrective Action
PID	Per Manual	Per Manual	Field Team Lead	Per Manual	Per Manual	Per Manual
DR-890	Per Manual	Per Manual	Field Team Lead	Per Manual	Per Manual	Per Manual
LaMotte Turbidometer 2020	Per Manual	Per Manual	Field Team Lead	Per Manual	Per Manual	Per Manual
pH Monitor (included with YSI)	Per Manual	Per Manual	Field Team Lead	Per Manual	Per Manual	Per Manual
YSI 600	Per Manual	Per Manual	Field Team Lead	Per Manual	Per Manual	Per Manual
Hach SRB-BART kit	Per SOP DOC316.53.01326	Per SOP DOC316.53.01326	Field Team Lead	Per SOP DOC316.53.01326	Per SOP DOC316.53.01326	Per SOP DOC316.53.01326
Hach 8203 kit (alkalinity)	Per SOP DOC316.53.01166	Per SOP DOC316.53.01166	Field Team Lead	Per SOP DOC316.53.01166	Per SOP DOC316.53.01166	Per SOP DOC316.53.01166
Hach Model IR-18C (ferrous iron)	Per SOP 26672-88	Per SOP 26672-88	Field Team Lead	Per SOP 26672-88	Per SOP 26672-88	Per SOP 26672-88

The above manuals are kept within the project files and can be found at the below links:

- PID - http://www.raesystems.com/sites/default/files/downloads/FeedsEnclosure-MiniRAE3000_Pocket_Reference_0.pdf
- DR-890 – http://www.hach.com/asset-get.download-en.jsa?id=7639982262
- LaMotte Turbidometer 2020 - http://www.lamotte.com/images/pdf/instructions/1970-MN.pdf
- YSI 600 - https://www.ysi.com/media/pdfs/069300-YSI-6-Series-Manual-RevH.pdf

The SOPs listed above are included as attachments to this UFP-QAPP.

QAPP Worksheet #23: Analytical SOPs

Laboratory must have current NELAC and/or New Jersey certification. The following Analytical SOPs are included as Attachment 2 of this UFP-QAPP.

SOP#	Title, Revision Date, and/or Number[1]	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
EAT004-08	Laboratory Analysis of Dissolved Gases in Aqueous Samples Rev.8 4/29/13	Definitive	Dissolved Gases	GC/FID/TCD	Accutest Laboratories, Dayton, NJ	No
EGN281-11	Determination of Inorganic Anions by Ion Chromatography using IC2000 Rev 11 7/18/2011	Definitive	Inorganic	Dionex ICS 2000	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No
EGCGRO801 5C-03	Total Volatile Petroleum Hydrocarbons Rev 3 6/20/2013	Definitive	Volatiles GC	Gas Chromatograph with FID detector HP, Agilent various models	Accutest Laboratories New Jersey, Inc., Dayton, NJ	No
EGCDRO801 5C-03	Total Semivolatile Petroleum Hydrocarbons Rev 3 6/19/2013	Definitive	Semivolatiles GC	Gas Chromatograph with dual FID detector HP, Agilent various models	Accutest Laboratories New Jersey, Inc., Dayton, NJ	No
EMA227	Metals: ICP Emission Spec. SW846 6010C Rev 6 9/10/12	Definitive	SW-846 6010C: Inductively Coupled Plasma-Atomic Emission Spectormetry	Thermo 6500 Solid State ICP	Accutest Laboratories New Jersey, Inc., Dayton, NJ	No
EMA226-07	Metals by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) Rev 7 4/12/13	Definitive	Inorganic	Agilent 7700X	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No
EMP070-15	Digestion of Non-Potable Waters for ICP or ICP-MS Analysis Rev 15 8/8/13	Definitive	Inorganic	Digestion Block	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No
EGN118-09	Sulfide Rev9 06/06/2013	Definitive	Inorganic	None	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No
EGN037-10	Alkalinity, Total Rev 10 10/07/2013	Definitive	Inorganic	pH Meter	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No

SOP#	Title, Revision Date, and/or Number[1]	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
EGN234-14	Total Organic Carbon in Aqueous Samples (TOC) Rev14 06/24/2013	Definitive	Inorganic	Shimadzu 5000 TOC Analyzer	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No
EGN310-03	Orthophosphate Rev3 06/24/2013	Definitive	Inorganic	Spectrophotometer	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No
EGN243-08	Ferrous Iron Rev8 06/12/2013	Definitive	Inorganic	Spectrophotometer	Accutest Laboratories New Jersey, Inc. Dayton, NJ	No
NA	Sulfur-Isotope Analysis by Ion Exchange*	Specialty	Inorganic	Colorimeter	Isotech Laboratories, Inc., Champaign, IL	NA
NA	Total Iron, Arsenic and Sulfur by XRF, Bulk and Clay Mineral Fractions by XRD, Pore System and Distribution of Matrix and Cement Constituents by SEM*	Specialty	Inorganic	SRF, XRD	Mineralogy, Inc., Tulsa, OK	NA

* data for these specialty analyses will not be validated

QAPP Worksheet #24: Analytical Instrument Calibration

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 Quality Control	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Dionex ICS-2000	Initial Multi point calibration, min 5 pts	Monthly	Correlation Coefficient R ≥ 0.995	Instrument Maintenance, standard inspection, recalibration	Laboratory Analyst	EGN281-11
	Continuing Calibration	Daily, every 10 samples	% Diff <10%			
Gas Chromatograph with FID detector HP, Agilent various models	Initial multi point calibration , minimum 5 pts	As needed	RPD < 20%	Instrument maintenance, standard, inspection, recalibration	Laboratory Analyst	EGCGRO8015C -03
	Calibration Verification	After initial	< 20% Diff			
	Continuing Calibration	Daily, every 12 hours or 10 samples	< 20% Diff			
Gas Chromatograph with dual FID detector HP, Agilent various models	Initial multi point calibration , minimum 5 pts	As needed	RPD < 20%	Instrument maintenance, standard, inspection, recalibration	Laboratory Analyst	EGCDRO8015C -03
	Calibration Verification	After initial	< 20% Diff			
	Continuing Calibration	Daily, every 12 hours or 10 samples	< 20% Diff			
Thermo 6500 ICP	Initial Blank + 3 non zero std's	Daily	Correlation Coefficient R ≥ 0.998	Instrument maintenance, standard, inspection, recalibration	Laboratory Analyst	EMA227

Instrument	Calibration Procedure	Frequency of Quality Control	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
	ICV	Beginning of run	≤ 10% Diff			
	CCV	Beginning of run, every 10 samples and end of run	≤ 10% Diff			
Agilent 7700 ICPMS	Tune	Every 1-2 days	RSD of min 4 replicates < 5% for all elements in tune solution Resolution < 0.9 amu full width at 10% peak height Mass Calibration < 0.1 amu	Retune Instrument	Laboratory Analyst	EMA226
	Initial cal, blank + 3 non zero standards	Daily	R > 0.995	Perform Instrument Maintenance, Check or reprep Standards, Recalibrate instrument		
	Initial Calibration Verification (Second Source Standard)	After ICAL	+ 10% of true value	Reanalyze ICV, Recalibrate instrument		
	Continuing Calibration Verification	After ICV, every 10 samples and end of run	+ 10% of true value	Reanalyze CCV, Recalibrate & Reanalyze affected samples		
	Low Level Calibration Check	After ICV and end of run	+ 20% of true value	Reanalyze LLCC , Perform Instrument Maintenance, Check or reprep Standards, Recalibrate instrument		
	Interference Check Standard (ICSA/ICASB)	After CCV, and every 12 hours	ICSA < LOD ICSAB +/- 20% of true value	Rerun ICSA/ICSAB, and all affected samples		

Instrument	Calibration Procedure	Frequency of Quality Control	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
pH Meter	pH 4, 7, and 10 buffer	Prior to analysis	±0.05 pH units	Clean, replace probe, replace standards, recalibration	Laboratory Analyst	EGN037-10
	pH 4 buffer	every 10 samples	±0.20 pH units			
HP5890 II	Initial: 5-points Minimum	Major maintenance (per method) or second consecutive failure of opening CCV warrants recalibration	ICAL %RSD <30%,	Instrument maintenance, leak check, standard inspection, recalibration	Laboratory Analyst	EAT004-07
	Continuing Calibration	at beginning, every 15 samples, and end of run	CCV %D <15%			
Spectrophotometer	Blank and 7	Required Quarterly	Corr Coeff > 0.995	Reprep standards, recalibrate	Laboratory Analyst	EGN243-08
	Blank, low std, high std	Daily	+/- 10%			
Spectrophotometer	Blank and 7	Required Quarterly	Corr Coeff > 0.995	Reprep standards, recalibrate	Laboratory Analyst	EGN310-03
	Blank, low std, high std	Daily	High Std+/- 10% Low Std +/- 30%			
Shimadzu TOC Analyzer	Initial: Blank + 5 standards	Required Quarterly	Correlation Coefficient > 0.995	Instrument Maintenance, standard inspection, recalibration	Laboratory Analyst	EGN234-14
	Blank, low std, high std	Daily	High Std+/- 10% Low Std +/- 30%			

Instrument	Calibration Procedure	Frequency of Quality Control	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Colorimeter*	Per internal laboratory procedures			NA	Laboratory Analyst	NA
XRF, XRD*	Per internal laboratory procedures			NA	Laboratory Analyst	NA

* data for these specialty analyses will not be validated

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

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Dionex ICS-2000	Replace Pump Tubing, Regenerate Suppressor, Clean/ Replace Columns	EPA 300.0 Inorganic ions	He Tank Pressure, Water level, Flow rate, KOH molarity	Daily	Acceptable Calibration Check	Perform Maintenance, Check Standards, Recalibrate, Reanalyze	Laboratory Analyst	EGN281-11
Gas Chromatograph with FID detector HP, Agilent various models	Clean &Bake Trap, purge tube, transfer lines, clip column	SW-846 8015 GRO	Check for leaks, review chromatography	Daily or as needed	Passing calibration	Perform maintenance, check standards, recalibrate	Laboratory Analyst	EGCGRO8015C-03
Gas Chromatograph with dual FID detector HP, Agilent various models	Clean injection port, change septa, clip/replace column	SW-846 8015 DRO	Check for leaks, review chromatography	Daily or as needed	Passing calibration	Perform maintenance, check standards, recalibrate	Laboratory Analyst	EGCDRO8015C-03
Thermo 6500 ICP	Torch, nebulizer, spray chamber, autosampler, pump tubing maintenance	SW-846 6010C	Check connections, flush lines, clean nebulizer	Daily or as needed	Passing calibration	Perform maintenance, check standards, recalibrate	Laboratory Analyst	EMA 207
Agilent 7700X	Clean/replace torch, Clean Cone, Clean/replace nebulizer, change pump tubing	SW846 6020A	Rf Generator power, nebulizer pressure, turbopump speed	Daily as needed	Passing tune, ICV and CCV	Perform Maintenance, Check Standards, Recalibrate, Reanalyze	Laboratory Analyst	EMA 226
pH Meter	Clean probe	Alkalinity	Inspect probe	Daily	Acceptable Calibration	Perform Maintenance, Check Standards, Recalibrate	Laboratory Analyst	EGN037-10

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
HP5890 II	Injector port, column maintenance	RSK175	Leak test, column and injector port inspection	As needed	Passing CCV	Column clipping, seals and liners replacement, recalibrate and reanalyze affected samples	Laboratory Analyst	EAT004-07
Spectrophotometer	Replace light bulb as needed	Ferrous iron	Daily calibration	Daily	Acceptable Calibration	Reprep Standards, Recalibrate	Laboratory Analyst	EGN243-08
Spectrophotometer	Replace light bulb as needed	Orthophosphate	Daily calibration	Daily	Acceptable Calibration	Reprep Standards, Recalibrate	Laboratory Analyst	EGN310-03
Shimadzu TOC Analyzer	Changing catalyst, air and water lines as needed	TOC, DOC	Check Water Level, O2 Pressure, Carrier Gas Pressure	Daily	Acceptable Calibration Check	Perform Maintenance, Check Standards, Recalibrate	Laboratory Analyst	EGN234-14
Colorimeter*		Per internal laboratory procedures			Laboratory Analyst		NA	
XRF, XRD*		Per internal laboratory procedures			Laboratory Analyst		NA	

* data for these specialty analyses will not be validated

QAPP Worksheet #26 and #27: Sample Handling, Custody, and Disposal

Sampling organization: Various

Laboratory: Accutest, Mineralogy Inc., Isotech Laboratories, Inc

Method of sample delivery (shipper/carrier): Federal Express—Priority Overnight

Number of days from reporting until sample disposal: Minimum 30 days after final report sent to the client

Activity	Organization and Title or Position of Person Responsible for the Activity	SOP Reference
Sample labeling	Field Team Lead, CH2M HILL	As Per COC SOP (attached)
Chain-of-custody form completion	Field Team Lead, CH2M HILL	As Per COC SOP (attached)
Packaging	Field Team Lead, CH2M HILL	As Per Packaging and Shipping Procedures SOP (attached)
Shipping coordination	Field Team Lead, CH2M HILL	As Per Packaging and Shipping Procedures SOP (attached)
Sample receipt, inspection, and log-in	Nick Popow, Supervisor, Receiving/Accutest	Accutest SOP# EPM004-04
Sample custody and storage	Dave Hukele, Sample Custodian/Accutest	Accutest SOP# ESM001-09
Sample disposal	Robert MacLean, Accutest	Accutest SOP# EHS004-04

Collecting data of known quality begins at the point of sample collection. Legally defensible data are generated by adhering to proven evidentiary procedures. These procedures are outlined in the following sections and must be followed to preserve and ensure the integrity of all samples from the time of collection through analysis. Sample custody records must be maintained both in the field and in the subcontractor laboratory. A sample is considered to be in someone's custody if it is either in his or her physical possession or view, locked up, or kept in a secured and restricted area. Until shipment, sample custody will be the responsibility of the sampling team leader.

Chain-of-custody records document sample collection and shipment to the laboratory. A chain-of-custody form will be completed for each sampling event. The original copy will be provided to the laboratory with the sample shipping cooler, and a copy will be retained in the field documentation files. The chain-of-custody form will identify the contents of each shipment and maintain the custodial integrity of the samples. All chain-of-custody forms will be signed and dated by the responsible sampling team personnel. The "relinquished by" box will be signed by the responsible sampling team personnel, and the date, time, and air bill number will be noted on the chain-of-custody form. The laboratory will return the executed copy of the chain-of-custody with the hardcopy report.

The shipping coolers containing the samples will be sealed with a custody seal any time the coolers are not in an individual's possession or view before shipping. All custody seals will be signed and dated by the responsible sampling team personnel.

At a minimum, the chain-of-custody form must contain:

- Site name.
- Project Manager, Project Chemist, and Data Manager names, telephone numbers, and fax numbers.
- Unique sample identification.
- Date and time of sample collection.
- Source of sample (including name, location, sample type, and matrix).
- Number of containers.
- Designation of MS/MSD.
- Preservative used.
- Analyses required.
- Name of sampler.
- Custody transfer signatures and dates and times of sample transfer from the field to transporters and to the laboratories.
- Bill of lading or transporter tracking number (if applicable).
- Turnaround time.
- Lab name, address, and contact information.
- Any special instructions.

Erroneous entries on chain-of-custody records will be corrected by drawing a line through the error and entering the corrected information. The person performing the correction will date and initial each change made on the chain-of-custody form.

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal): A custodian at the laboratory will accept custody of the shipped samples, and check them for discrepancies, proper preservation, integrity, etc. If noted, issues will be forwarded to the laboratory project or laboratory manager for corrective action; Earth Tech will be notified and will be involved in decisions on corrective action. The sample custodian will relinquish custody to the appropriate department for analysis. A “Condition upon Receipt” or similar form will be completed by the laboratory and will be included in the analytical data package.

Disposal of the samples will occur only after analyses and QA/QC checks are completed, and 60 days after issuance of analytical report.

STANDARD OPERATING PROCEDURE

Chain-of-Custody

I Purpose

The purpose of this SOP is to provide information on chain-of-custody procedures to be used for project work.

II Scope

This procedure describes the steps necessary for transferring samples through the use of Chain-of-Custody Records. A Chain-of-Custody Record is required, without exception, for the tracking and recording of samples collected for on-site or off-site analysis (chemical or geotechnical) during program activities (except wellhead samples taken for measurement of field parameters). Use of the Chain-of-Custody Record Form creates an accurate written record that can be used to trace the possession and handling of the sample from the moment of its collection through analysis. This procedure identifies the necessary custody records and describes their completion. This procedure does not take precedence over region specific or site-specific requirements for chain-of-custody.

III Definitions

Chain-of-Custody Record Form - A Chain-of-Custody Record Form is a printed two-part form that accompanies a sample or group of samples as custody of the sample(s) is transferred from one custodian to another custodian. One copy of the form must be retained in the project file.

Custodian - The person responsible for the custody of samples at a particular time, until custody is transferred to another person (and so documented), who then becomes custodian. A sample is under one's custody if:

- It is in one's actual possession.
- It is in one's view, after being in one's physical possession.
- It was in one's physical possession and then he/she locked it up to prevent tampering.
- It is in a designated and identified secure area.

Sample - A sample is physical evidence collected from a facility or the environment, which is representative of conditions at the point and time that it was collected.

IV. Procedures

The term "chain-of-custody" refers to procedures which ensure that evidence presented in a court of law is valid. The chain-of-custody procedures track the evidence from the time and place it is first obtained to the courtroom, as well as providing security for the evidence as it is moved and/or passed from the custody of one individual to another.

Chain-of-custody procedures, recordkeeping, and documentation are an important part of the management control of samples. Regulatory agencies must be able to provide the chain-of-possession and custody of any samples that are offered for evidence, or that form the basis of analytical test results introduced as evidence. Written procedures must be available and followed whenever evidence samples are collected, transferred, stored, analyzed, or destroyed.

Sample Identification

The method of identification of a sample depends on the type of measurement or analysis performed. When *in situ* measurements are made, the data are recorded directly in bound logbooks or other field data records with identifying information.

Information which shall be recorded in the field logbook, when in-situ measurements or samples for laboratory analysis are collected, includes:

- Field Sampler(s),
- Contract Number,
- Project Sample Number,
- Sample location or sampling station number,
- Date and time of sample collection and/or measurement,
- Field observations,
- Equipment used to collect samples and measurements, and
- Calibration data for equipment used

Measurements and observations shall be recorded using waterproof ink.

Sample Label

Samples, other than for *in situ* measurements, are removed and transported from the sample location to a laboratory or other location for analysis. Before removal, however, a sample is often divided into portions, depending upon the analyses to be performed. Each portion is preserved in accordance with the Sampling and Analysis Plan. Each sample container is identified by a sample label (see Attachment A). Sample labels are provided, along with sample containers, by the analytical laboratory. The information recorded on the sample label includes:

- Project Number.
- Station Location - The unique sample number identifying this sample.
- Date - A six-digit number indicating the day, month, and year of sample collection (e.g., 08/21/12).

- Time - A four-digit number indicating the 24-hour time of collection (for example: 0954 is 9:54 a.m., and 1629 is 4:29 p.m.).
- Medium - Water, soil, sediment, sludge, waste, etc.
- Sample Type - Grab or composite.
- Preservation - Type and quantity of preservation added.
- Analysis - VOA, BNAs, PCBs, pesticides, metals, cyanide, other.
- Sampled By - Printed name of the sampler.
- Remarks - Any pertinent additional information.

Using only the work assignment number of the sample label maintains the anonymity of sites. This may be necessary, even to the extent of preventing the laboratory performing the analysis from knowing the identity of the site (e.g., if the laboratory is part of an organization that has performed previous work on the site). The field team should always follow the sample ID system prepared by the project EIS and reviewed by the Project Manager.

Chain-of-Custody Procedures

After collection, separation, identification, and preservation, the sample is maintained under chain-of-custody procedures until it is in the custody of the analytical laboratory and has been stored or disposed.

Field Custody Procedures

- Samples are collected as described in the site Sampling and Analysis Plan. Care must be taken to record precisely the sample location and to ensure that the sample number on the label matches the Chain-of-Custody Record exactly.

- A Chain-of-Custody Record will be prepared for each individual cooler shipped and will include ***only*** the samples contained within that particular cooler. The Chain-of-Custody Record for that cooler will then be sealed in a zip-log bag and placed in the cooler prior to sealing. This ensures that the laboratory properly attributes trip blanks with the correct cooler and allows for easier tracking should a cooler become lost during transit.

- The person undertaking the actual sampling in the field is responsible for the care and custody of the samples collected until they are properly transferred or dispatched.

- When photographs are taken of the sampling as part of the documentation procedure, the name of the photographer, date, time, site location, and site description are entered sequentially in the site logbook as photos are taken. Once downloaded to the server or developed, the electronic files or photographic prints shall be serially numbered, corresponding to the logbook descriptions; photographic prints will be stored in the project files. To identify sample

locations in photographs, an easily read sign with the appropriate sample location number should be included.

- Sample labels shall be completed for each sample, using waterproof ink unless prohibited by weather conditions (e.g., a logbook notation would explain that a pencil was used to fill out the sample label if the pen would not function in freezing weather.)

Transfer of Custody and Shipment

Samples are accompanied by a Chain-of-Custody Record Form. **A Chain-of-Custody Record Form must be completed for each cooler and should include only the samples contained within that cooler**. A Chain-of-Custody Record Form example is shown in Attachment B. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the Record. This Record documents sample custody transfer from the sampler, often through another person, to the analyst in the laboratory. The Chain-of-Custody Record is filled out as given below:

- Enter header information (project number, samplers, and project name).

- Enter sample specific information (sample number, media, sample analysis required and analytical method grab or composite, number and type of sample containers, and date/time sample was collected).

- Sign, date, and enter the time under "Relinquished by" entry.

- Have the person receiving the sample sign the "Received by" entry. If shipping samples by a common carrier, print the carrier to be used in this space (i.e., Federal Express).

- If a carrier is used, enter the airbill number under "Remarks," in the bottom right corner;

- Place the original (top, signed copy) of the Chain-of-Custody Record Form in a plastic zipper-type bag or other appropriate sample-shipping package. Retain the copy with field records.

- Sign and date the custody seal, a 1-inch by 3-inch white paper label with black lettering and an adhesive backing. Attachment C is an example of a custody seal. The custody seal is part of the chain-of-custody process and is used to prevent tampering with samples after they have been collected in the field. Custody seals shall be provided by the analytical laboratory.

- Place the seal across the shipping container opening (front and back) so that it would be broken if the container were to be opened.

- Complete other carrier-required shipping papers.

The custody record is completed using waterproof ink. Any corrections are made by drawing a line through and initialing and dating the change, then entering the correct information. Erasures are not permitted.

Common carriers will usually not accept responsibility for handling Chain-of-Custody Record Forms; this necessitates packing the record in the shipping container (enclosed with other documentation in a plastic zipper-type bag). As long as custody forms are sealed inside the shipping container and the custody seals are intact, commercial carriers are not required to sign the custody form.

The laboratory representative who accepts the incoming sample shipment signs and dates the Chain-of-Custody Record, completing the sample transfer process. It is then the laboratory's responsibility to maintain internal logbooks and custody records throughout sample preparation and analysis.

V Quality Assurance Records

Once samples have been packaged and shipped, the Chain-of-Custody copy and airbill receipt become part of the quality assurance record.

VI Attachments

A. Sample Label
B. Chain of Custody Form
C. Custody Seal

VII References

USEPA. *User's Guide to the Contract Laboratory Program*. Office of Emergency and Remedial Response, Washington, D.C. (EPA/540/P-91/002), January 1991.

Attachment A

Example Sample Label

QAL

Quality Analytical Laboratories, Inc.
2567 Fairlane Drive
Montgomery, Alabama 36116
PH. (334)271-2440

Client _____
Sample No. _____
Location _____
_____
Analysis _____
_____
Preservative HCL
Date _____ By _____

CEIMIC
CORPORATION
10 Dean Knauss Drive, Narragansett, R.I. 02882 • (401) 782-8900

SITE NAME	DATE
ANALYSIS	TIME
	PRESERVATIVE

SAMPLE TYPE

☐ Grab ☐ Composite ☐ Other _____

COLLECTED BY:

Attachment B

Example Chain-of-Custody Record

CH2M HILL
APPLIED SCIENCES LABORATORY

CHAIN OF CUSTODY RECORD AND AGREEMENT TO PERFORM SERVICES

CH2M Hill Project #: ☐☐☐☐☐☐☐☐.☐☐.☐☐

Purchase Order #:

Project Name:

Company Name CH2M HILL Office:

Project Manager & Phone #:
Mr. [ ]
Ms. [ ]
Dr. [ ]

Report Copy to:

Requested Completion Date:

Sampling Requirements: SDWA ☐ NPDES ☐ RCRA ☐ OTHER ____

Sample Disposal: Dispose ☐ Return ☐

Sampling Date	Sampling Time	Type: COMP	Type: GRAB	Matrix: WATER	Matrix: SOIL	Matrix: AIR	CLIENT SAMPLE ID (9 CHARACTERS)	# OF CONTAINERS	LAB TEST CODES	ANALYSES REQUESTED	REMARKS	LAB 1 ID	LAB 2 ID

SHADED AREA– FOR LAB USE ONLY

Lab 1 #	Lab 2 #
Quote #	Kit Request #
Project #	
No. of Samples	Page of
Login	LIMS Ver

Sampled By & Title (Please sign and print name)	Date/Time	Relinquished By (Please sign and print name) — Date/Time
Received By (Please sign and print name)	Date/Time	Relinquished By (Please sign and print name) — Date/Time
Received By (Please sign and print name)	Date/Time	Relinquished By (Please sign and print name) — Date/Time
Received By (Please sign and print name)	Date/Time	Shipped Via: UPS BUS Fed-Ex Hand Other ____ — Shipping #
Work Authorized By (Please sign and print name)	Remarks	

QC Level: 1 2 3 Other: ____

COC Rec	ICE
Ana Req	TEMP
Cust Seal	Ph

Instructions and Agreement Provisions on Reverse Side

DISTRIBUTION: Original - LAB, Yellow - LAB, Pink - Client

REV 3/94 FORM 340

Attachment C

Example Custody Seal

CH2M HILL

CUSTODY SEAL

Date

Signature

STANDARD OPERATING PROCEDURE

Packaging and Shipping Procedures for Samples

I. Purpose and Scope

The purpose of this guideline is to describe the packaging and shipping of samples of various media to a laboratory for analysis.

II. Scope

The guideline only discusses the packaging and shipping of samples that are anticipated to have non-hazardous concentrations of chemical constituents. Whether or not samples should be classified as low-concentration or otherwise will depend upon the site history, observation of the samples in the field, odor, and photoionization-detector readings.

If the site is known to have produced high-concentration samples in the past or the sampler suspects that high concentrations of contaminants might be present in the samples, then the sampler should conservatively assume that the samples cannot be classified as low-concentration. Samples that are anticipated to have medium to high concentrations of constituents should be packaged and shipped accordingly.

If warranted, procedures for dangerous-goods shipping may be implemented. Dangerous goods and hazardous materials pose an unreasonable risk to health, safety, or property during transportation without special handling. As a result only employees who are trained under CH2M HILL Dangerous Goods Shipping course may ship or transport dangerous goods. Employees should utilize the HAZMAT ShipRight tool on the Virtual Office and/or contact a designated CH2M HILL HazMat advisor with questions.

III. Equipment and Materials

- Coolers
- Clear tape
- “This Side Up” labels
- “Fragile” labels
- Vermiculite
- Ziplock bags or bubble wrap
- Ice
- Chain-of-Custody form (completed)
- Custody seals

IV. Procedures and Guidelines

Low-Concentration Samples

A. Prepare coolers for shipment:

- Tape drains shut.
- Affix "This Side Up" labels on all four sides and "Fragile" labels on at least two sides of each cooler.
- Place mailing label with laboratory address on top of coolers.
- Fill bottom of coolers with about 3 inches of vermiculite or absorbent pads.

B. Arrange decontaminated sample containers in groups by sample number. Consolidate VOC samples into one cooler to minimize the need for trip blanks.

C. Affix appropriate adhesive sample labels to each container. Protect with clear label protection tape.

D. Seal each sample bottle within a separate ziplock plastic bag or bubble wrap, if available. Tape the bag around bottle. Sample label should be visible through the bag.

E. Arrange sample bottles in coolers so that they do not touch.

F. If ice is required to preserve the samples, cubes should be repackaged in zip-lock bags and placed on and around the containers.

G. Fill remaining spaces with vermiculite or absorbent pads.

H. Complete and sign chain-of-custody form (or obtain signature) and indicate the time and date it was relinquished to Federal Express or the courier.

J Close lid and latch.

K. Carefully peel custody seals from backings and place intact over lid openings (right front and left back). Cover seals with clear protection tape.

L. Tape cooler shut on both ends, making several complete revolutions with strapping tape. Cover custody seals with tape to avoid seals being able to be peeled from the cooler.

M. Relinquish to Federal Express or to a courier arranged with the laboratory. Place airbill receipt inside the mailing envelope and send to the sample documentation coordinator along with the other documentation.

Medium- and High-Concentration Samples:

Medium- and high-concentration samples are packaged using the same techniques used to package low-concentration samples, with potential additional restrictions. If applicable, the sample handler must refer to instructions associated with the shipping of dangerous goods for the necessary procedures for shipping by Federal Express or other overnight carrier. If warranted, procedures for dangerous-goods shipping may be implemented. Dangerous goods and hazardous materials pose an unreasonable risk to health, safety, or property during transportation without special handling. As a result only employees who are trained under CH2M HILL Dangerous Goods Shipping course may ship or transport dangerous goods. Employees should utilize the HAZMAT ShipRight tool on the Virtual Office and/or contact a designated CH2M HILL HazMat advisor with questions.

V. Attachments

None.

VI. Key Checks and Items

- Be sure laboratory address is correct on the mailing label
- Pack sample bottles carefully, with adequate vermiculite or other packaging and without allowing bottles to touch
- Be sure there is adequate ice
- Include chain-of-custody form
- Include custody seals

QAPP Worksheet #28: Analytical Quality Control and Corrective Action

Matrix: Aqueous

Analytical group: TPH—DRO/GRO

Analytical method/SOP: SW8015B/ EGCGRO8015C-03 and EGCDRO8015C-03; RSK-175/EAT004-08

TABLE 28-3

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
Initial Calibration	Prior to sample analysis	If the %RSD is ≤ 20%, the average RRF may be used for quantitation; otherwise use calibration curve with coefficient of correlation or determination ≥ 0.99.	Check instrument, recalibrate; qualify data	Lab personnel	RSD ≤ 20% of average RRF
Continuing calibration check standard	At the start of each analytical sequence and after every 10 samples, and at the end of the sequence.	Analytes within ±20% of true value	Recalibrate, qualify data	Lab personnel	±20% of true value
Method Blank (Lab Reagent Blank)	At least one per analytical batch	< RL	Identify source and correct prior to continuing analysis	Lab personnel	< RL
MS/MSD	1 per 20 samples	70-130 %R	Assume matrix bias; qualify data; note in case narrative	Lab personnel	70-130% R; RPD ≤ 20%
LCS/LCSD	At least one per analytical batch	70 – 130% R; RPD ≤ 20%	Qualify data unless high recovery and/or not detected	Lab personnel	70 – 130% R; RPD ≤ 20%
Surrogate Compounds	all samples, standards, and blanks	70–130% R	Reinject; qualify data	Lab personnel	70–130% R

[a] Recovery and precision limits and measurement performance criteria are generic.

Matrix: Aqueous

Analytical group: Metals

Analytical method/SOP: SW6010C/ EMA227

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
Initial calibration (a blank and at least one standard)	Before sample analysis, every 24 hours, whenever modifications are made to the system, or when continuing calibration verification fails.	If more than one standard is used, correlation coefficient must be > 0.995.	Recalibrate	Laboratory personnel	correlation coefficient > 0.995.
Initial Calibration Verification (ICV)	After each calibration	90% - 110%	Check instrument; reanalyze	Laboratory personnel	90% - 110%
Initial Calibration Blank (ICB)	After ICV	< RL	Investigate source of contamination	Laboratory personnel	< RL
Continuing Calibration Verication (CCV)	After every 10 samples and at the end of the analysis sequence.	90% - 110%	Check instrument; reanalyze	Laboratory personnel	90% - 110%
Continuing Calibration Blank (CCB)	After every CCV	< RL	Investigate source of contamination	Laboratory personnel	< RL
Method Blank	At least one per analytical batch.	< RL	Investigate source of contamination	Laboratory personnel	< RL
MS/MSD	1 per 20 samples	80-120%R*	Qualify data	Laboratory personnel	80-120%R; RPD ≤ 20%
Low Level Check Std	Beginning and end of each analytical run	± 50 % of true value	Check instrument; recalibrate	Laboratory personnel	± 50 % of true value
Serial Dilution	Matrix spike sample	RPD < 10%	Qualify data	Laboratory personnel	RPD < 10%
Post Digestion Spike	Matrix spike sample	85-115%R	Qualify data	Laboratory personnel	85-115%R
Laboratory sample duplicate	Once per analytical batch if MSD or LCSD not performed.	RPD ≤20%	None.	Laboratory personnel	RPD ≤20%
Interference Check Sample	beginning, and end of each analytical run	All analytes within ±20% of expected value.	As per SOP	Laboratory personnel	All analytes within ±20% of expected value.

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
Laboratory Control Sample (LCS)/LCSD	At least one per analytical batch.	80-120%; RPD < 20%	Qualify data	Laboratory personnel	80-120% R; RPD ≤ 20%

[a] Recovery and precision limits and measurement performance criteria are generic.

Matrix: Aqueous

Analytical group: Metals

Analytical method/SOP: SW6020/ EMA226-07

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
Tune criteria	Prior to initial calibration	Must meet the method tune criteria prior to beginning analytical sequence	Retune and reanalyze tune solution	Laboratory personnel	Per method
Initial calibration (a blank and at least one standard)	Before sample analysis, every 24 hours, whenever modifications are made to the system, or when continuing calibration verification fails.	If more than one standard is used, correlation coefficient must be > 0.995.	Recalibrate	Laboratory personnel	correlation coefficient > 0.995.
Initial Calibration Verification (ICV)	After each calibration	90% - 110%	Check instrument; reanalyze	Laboratory personnel	90% - 110%
Initial Calibration Blank (ICB)	After ICV	< RL	Investigate source of contamination	Laboratory personnel	< RL
Continuing Calibration Verication (CCV)	After every 10 samples and at the end of the analysis sequence.	90% - 110%	Check instrument; reanalyze	Laboratory personnel	90% - 110%
Continuing Calibration Blank (CCB)	After every CCV	< RL	Investigate source of contamination	Laboratory personnel	< RL
Method Blank	At least one per analytical batch.	< RL	Investigate source of contamination	Laboratory personnel	< RL
MS/MSD	1 per 20 samples	80-120%R*	Qualify data	Laboratory personnel	80-120%R; RPD ≤ 20%
Low Level Check Std	Beginning and end of each analytical run	± 50 % of true value	Check instrument; recalibrate	Laboratory personnel	± 50 % of true value
Serial Dilution	Matrix spike sample	RPD < 10%	Qualify data	Laboratory personnel	RPD < 10%
Post Digestion Spike	Matrix spike sample	85-115%R	Qualify data	Laboratory personnel	85-115%R
Laboratory sample duplicate	Once per analytical batch if MSD or LCSD not performed.	RPD ≤20%	None.	Laboratory personnel	RPD ≤20%

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
Interference Check Sample	beginning, and end of each analytical run	All analytes within ±20% of expected value.	As per SOP	Laboratory personnel	All analytes within ±20% of expected value.
Internal Standards	Each sample	Internal standard intensity >70% of intensity of initial standard in the initial calibration Internal standard should be within 50 atomic mass units of the associated target analyte	Perform corrective action as described in the method	Laboratory personnel	Per method
Laboratory Control Sample (LCS)/LCSD	At least one per analytical batch.	80-120%; RPD < 20%	Qualify data	Laboratory personnel	80-120% R; RPD ≤ 20%

[a] Recovery and precision limits and measurement performance criteria are generic.

Matrix: Aqueous

Analytical group: General Chemistry

Analytical method/SOP: SW9060/EGN234-14; SM4500-PE/EGN310-03; SM4500-Fe/EGN243-08; E300.0/ EGN281-11; SM4500S2-D/ EGN118-09; SM2320B/ EGN037-10

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
Initial Calibration (Multi-Point only) (not for SM2320B)	Daily initial calibration prior to sample analysis	Correlation Coefficient < 0.995 %RSD <10% for any analyte	If applicable, correct problem and repeat initial calibration.	Laboratory personnel	Correlation Coefficient < 0.995 %RSD <10% f
Initial Calibration Verification (ICV) (not for SM2320B)	After each calibration; every 10 samples; end of each analytical run	90% - 110% 85%-115% for SW9060	Check instrument; reanalyze	Laboratory personnel	90% - 110% 85%-115% for SW9060
Continuing Calibration Verification (CCV) (not for SM2320B)	After every 10 samples and at the end of the analysis sequence	90% - 110% 85%-115% for SW9060	Reanalyze; qualify data	Laboratory personnel	90% - 110% 85%-115% for SW9060
Calibration blank (not for SM2320B)	Before beginning a sample run and after every calibration verification	all constituents < RL	Investigate source of contamination	Laboratory personnel	all constituents < RL
Method Blank	At least one per analytical batch	all constituents < RL	Investigate source of contamination	Laboratory personnel	all constituents < RL
MS/MSD	1 per 20 samples	80-120%R*	Qualify data	Laboratory personnel	80-120%R; RPD ≤ 20%
Retention Time Window (E300.0 only)	Each analyte.	Analyte within established window	Not applicable (used for identification of analyte).	Laboratory personnel	Analyte within established window
Lab Duplicate	At least one per analytical batch if no MSD or LSCD analyzed	RPD ≤ 20%	Reanalyze. If still unacceptable, flag all associated data in the analytical batch.	Lab Duplicate	RPD ≤ 20%
Laboratory Control Sample (LCS)/LCSD	At least one per analytical batch	80-120%; RPD < 20%	Qualify data	Laboratory personnel	80-120% R; RPD ≤ 20%

[a] Recovery and precision limits and measurement performance criteria are generic.

Matrix: Aqueous

Analytical group: Sulfur Isotope

Analytical method/SOP: Ion Exchange*

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
NA	NA	NA	NA	NA	NA

[a] A laboratory SOP does not exist for this method and data will not be validated.

Matrix: Sediment

Analytical group: Total Iron, Arsenic and Sulfur, Bulk and Clay Mineral Fractions, Pore System and Distribution of Matrix and Cement Constituents

Analytical method/SOP: XRF, XRD, SEM*

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC[a]
NA	NA	NA	NA	NA	NA

[a] A laboratory SOP does not exist for these analyses and data will not be validated.

QAPP Worksheet #29: Project Documents and Records

The electronic data will be used to generate validation reports, modeling results, data summary tables, maps, and other figures. This program will follow CH2M HILL standard procedures for environmental data collection.
Data collected during the field demonstrations will be reduced, reviewed, and a report on the findings will be tabulated in a standard format. The criteria used to identify and quantify the analytes will be those specified in the analytical methods. Data deliverables will be reported as "CLP-like" Sample Delivery Groups (SDGs). In addition, the USEPA shall have access to the lab and site data upon request.

The completed copies of the chain-of-custody records (both external and internal) accompanying each sample from time of initial bottle preparation to completion of analysis shall be attached to the analytical reports.

The Data Package will consist of SDGs in "PDF" format. The laboratory will upload the EDD directly to the project LocusFocus EIM database. The laboratory will provide the data package deliverables 21 business days after sample receipt of a complete sample delivery group. The Project Chemist (PC) will check the package to ensure all deliverables have been provided. If problems are identified, the laboratory will be alerted, and corrective actions will be requested. The data will be used to generate summary tables.

The electronic deliverable formats will be submitted according to the Honeywell EDD requirements. All deliverables must also undergo a QC check by the laboratory before delivery. The original data, tabulations, and electronic media are stored in a secure and retrievable fashion.

The Project Manager or Data Manager will maintain close contact with the PC to ensure all non-conformance issues are acted upon prior to data manipulation and assessment routines.

Data will be archived in project files and on electronic archive tapes for the duration of the project, 5 years, or as specified in contractual agreements.

The data flow from the laboratory and field to the project staff and data users will be sufficiently documented to ensure that data are properly tracked and reviewed before use.

In addition to the data management procedures, the laboratory will ensure that electronic and hardcopy records sufficient to recreate each analytical event are maintained. The minimum records the laboratory will keep contain the following:

- Raw data, including instrument printouts, bench work sheets, and/or chromatograms with compound identification and quantitation reports.
- Laboratory-specific written SOPs for each analytical method and QA/QC function in place at the time of analysis of project samples.
- Record keeping requirements for non-analytical data are included in the PDWP.

The below table lists field files and assessment reports that will be kept on file. Additional records will be kept on an as needed basis.

Sample Collection Documents and Records	On-site Analysis Documents and Records	Off-site Analysis Documents and Records	Data Assessment Documents and Records	Other
• Site and field logbooks • COC forms • Request forms and associated correspondence	• Field Analysis HACH Kits • Water quality parameters	• Internal COC forms • Sample preparation log • Standard traceability logs • Instrument calibration data • Instrument analysis logs • QC summary checklist with all relevant information • Sample analysis data • Instrument/computer printouts • Definition of qualifiers • Final report	• Sample acceptance checklist • Corrective action reports	• Telephone/email logs • Corrective action documentation • Equipment maintenance logs • Procurement request forms

QAPP Worksheets #31, #32, and #33: Assessments and Corrective Action

Assessments

Assessment Type	Responsible Party and Organization	Number/Frequency	Estimated Dates	Assessment Deliverable	Deliverable Due Date
Health and Safety Audit	Bill Berlett, Health and Safety Manager, CH2M HILL	Minimum of 1 per year	TBD	Audit checklist	TBD
QC Audit	Steve Martz/Kyle Block, Quality Control Manager, CH2M HILL	Minimum of 1 per year	TBD	Audit checklist	TBD
Laboratory Audit	Bernice Kidd, Project Chemist, CH2M HILL	As needed	N/A	Laboratory Audit Report	As needed

Assessment

Quality assurance audits may be performed by or under the direction of the project QM (Quality Manager). These audits will be implemented to evaluate the capability and performance of project and subcontractor personnel, items, activities, and documentation of the measurement system(s). The QM may plan, schedule, and approve system and performance audits based upon CH2M HILL SOP customized to the project requirements. At times, the QM may request additional personnel with specific expertise from company and/or project groups to assist in conducting performance audits. However, these personnel will not have responsibility for the project work associated with the performance audit.

System Audits

System audits, performed by the QM or designated auditors, will encompass a qualitative evaluation of measurement system components to ascertain their appropriate selection and application. In addition, field and laboratory quality control procedures and associated documentation may be system audited. These audits may be performed once during the performance of the project. However, if conditions adverse to quality are detected or if the Project Manager requests, additional audits may occur.

Performance Audits

The laboratory will be required to conduct an analysis of Performance Evaluation (PE) samples or provide proof that Performance Evaluation samples submitted by USEPA or a state agency have been analyzed within the past twelve (12) months.

Formal Audits

Formal audits refer to any system or performance audit that is documented and implemented by the QM. These audits encompass documented activities performed by qualified lead auditors to a written procedure or checklists to objectively verify that quality assurance requirements have been developed, documented, and instituted in accordance with contractual and project criteria. Formal audits may be performed on project and subcontractor work at various locations.

Auditors who have performed the site audit after gathering and evaluating all data will write audit reports. Items, activities, and documents determined by lead auditors to be in noncompliance shall be identified at exit interviews conducted with the involved management. Noncompliance's will be logged and documented through audit findings, which are attached to and are a part of the integral audit report. These audit-finding forms are directed to management to satisfactorily resolve the noncompliance in a specified and timely manner.

The Project Manager has overall responsibility to ensure that all corrective actions necessary to resolve audit findings are acted upon promptly and satisfactorily. Audit reports must be submitted to the Project Manager within fifteen days of completion of the audit. Serious deficiencies will be reported to the Project Manager within 24 hours. All audit checklists; audit reports, audit findings, and acceptable resolutions are approved by the QM prior to issue. Verification of acceptable resolutions may be determined by re-audit or documented surveillance of the item or activity. Upon verification acceptance, the QM will close out the audit report and findings.

Assessment Response and Corrective Action

Assessment Type	Responsibility for Responding to Assessment Findings	Assessment Response Documentation	Timeframe for Response	Responsibility for Implementing Corrective Action	Responsible for Monitoring Corrective Action Implementation
Health and Safety Audit	Steve Zarlinski, PM CH2M HILL	Letter and any verification documentation	24 hours after notification	Field Team Leader, CH2M HILL	Bill Berlett, Health and Safety Manager CH2M HILL
QC Audit	Steve Zarlinski, PM CH2M HILL	Letter and any verification documentation	24 hours after notification	Field Team Leader, CH2M HILL	Steve Martz/Kyle Block, Quality Control Manager CH2M HILL

Corrective Action

The following procedures have been established to ensure that conditions adverse to quality, such as malfunctions, deficiencies, deviations, and errors, are promptly investigated, documented, evaluated, and corrected. Corrective action forms are included in the PDWP.

Procedure Description

When a significant condition adverse to quality is noted at site, laboratory, or subcontractor location, the cause of the condition will be determined and corrective action will be taken to preclude repetition. Condition identification, cause, reference documents, and corrective action planned to be taken will be documented and reported to the QM, Project Manager, Field Team Leader and involved subcontractor management, at a minimum. Implementation of corrective action is verified by documented follow-up action.

All project personnel have the responsibility, as part of the normal work duties, to promptly identify, solicit approved correction, and report conditions adverse to quality. Corrective actions will be initiated as follows:

- When predetermined acceptance standards are not attained;
- When procedure or data compiled are determined to be deficient;
- When equipment or instrumentation is found to be faulty;

- When samples and analytical test results are not clearly traceable;
- When quality assurance requirements have been violated;
- When designated approvals have been circumvented;
- As a result of system and performance audits;
- As a result of a management assessment;
- As a result of laboratory/field comparison studies; and
- As required by USEPA and USEPA SW-846 Methods.

Project management and staff, such as field investigation teams, remedial response planning personnel, and laboratory groups, monitor on-going work performance in the normal course of daily responsibilities. Work may be audited at the CH2M HILL office, sites, laboratories, or subcontractor locations. Activities or documents ascertained to be noncompliant with quality assurance requirements will be documented. Corrective actions will be mandated through audit finding sheets attached to the audit report. Audit findings are logged, maintained, and controlled by the Task Manager.

Personnel assigned to quality assurance functions will have the responsibility to issue and control Corrective Action Request (CAR) forms (See PDWP). The CAR identifies the out-of-compliance condition, reference document(s), and recommended corrective action(s) to be administered. The CAR is issued to the personnel responsible for the affected item or activity. A copy is also submitted to the Project Manager. The individual to whom the CAR is addressed returns the requested response promptly to the QA personnel, affixing his/her signature and date to the corrective action block, after stating the cause of the conditions and corrective action to be taken. The QA personnel maintain the log for status of CARs, confirms the adequacy of the intended corrective action, and verifies its implementation. CARs will be retained in the project file for the records.

Any project personnel may identify noncompliance issues; however, the designated QA personnel are responsible for documenting, numbering, logging, and verifying the close out action. The Project Manager will be responsible for ensuring that all recommended corrective actions are implemented, documented, and approved.

Reports to Management

CH2M HILL management personnel receive QA reports appropriate to their level of responsibility. The PM receives copies of all QA documentation. QC documentation is retained within the department that generated the product or service except where this documentation is a deliverable for a specific contract. QC documentation is also submitted to the QM for review and approval. Previous sections detailed the QA activities and the reports that they generate. A final audit report for each project may also be prepared. The reports may include:

- periodic assessment of measurement data accuracy, precision, and completeness;
- results of performance audits and/or system audits;
- significant QA problems and recommended solutions for future projects; and
- status of solutions to any problems previously identified.

Additionally, any incidents requiring corrective action will be fully documented.

QAPP Worksheet #34: Data Verification and Validation Inputs

Verification Input	Description	Internal/External	Responsible for Verification (Name, Organization)
Field Notes	Field notes will be reviewed internally and placed in the site file. A copy of the field notes will be attached to the final report.	Internal	FTL, CH2M HILL
COC and shipping forms	COC and shipping forms will be reviewed internally upon completion and verified against the packed coolers they represent. The shippers' signature on the COC should be initialed by the reviewer, a copy of the COC retained in the site file, and the original and remaining copies taped inside the cooler for shipment.	Internal	FTL, CH2M HILL
Audit Report	Upon report completion, a copy of all audit reports will be placed in the site file. If CAs are required, a copy of the documented CA taken will be attached to the appropriate audit report in the site file. At the beginning of each week and at the completion of the site work, site file audit reports will be reviewed internally to ensure that all appropriate CAs have been taken and that CA reports are attached. If CAs have not been taken, the Site Manager will be notified to ensure no action is taken.	Internal	Steve Zarlinski, PM, CH2M HILL
Laboratory Data	All laboratory data packages will be verified externally by the laboratory performing the work for completeness and technical accuracy prior to submittal.	External	Accutest (Kristin Beebe) Isotech Laboratories (Alan Langenfield)* Mineralogy, Inc. (Timothy Murphy)*

* data for these specialty analyses will not be validated

QAPP Worksheet #35: Data Verification Procedures

Step IIa/IIb	Validation Input	Description	Person(s) Responsible for Validation
IIa	Field SOPs	Verify that the sampling SOPs were followed	Mike Murphy, FTL, CH2M HILL
IIa	Analytical SOPs	Verify that the analytical SOPs were followed	Laboratory QA Officer/TBD Berney Kidd/CH2M HILL
IIa	Method QC Results	Verify that the required QC samples were run and met required limits	Laboratory QA Officer/TBD Berney Kidd/CH2M HILL
IIa/IIb	Data Validation	Validate 100 percent of the data to confirm quality	Berney Kidd/CH2M HILL
IIa/IIb	Data Usability Evaluation	Evaluate data based on precision, accuracy, representativeness, comparability and completeness for project objectives	Berney Kidd/CH2M HILL
IIb	Onsite Screening (such as PID readings)	Verify that the field data meets Work Plan requirements for completeness and accuracy based on field calibration records	Mike Murphy, FTL, CH2M HILL
IIb	Field Documentation	Verify accuarcy and completenss of field notes	Mike Murphy, FTL, CH2M HILL
IIb	Field QC Sample Results	Verify that the required field QC samples were run and met required limits	Laboratory QA Officer/TBD Berney Kidd/CH2M HILL

QAPP Worksheet #36: Data Validation Procedures

TABLE 36-1
Data Validation Procedures

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (Title and Organizational Affiliation)
IIa/IIb	Soil/Sediment	All methods with exceptions noted within QAPP	Low	Defined below	Berney Kidd/CH2M HILL Peeyush Gupta/HTS
IIa/IIb	Groundwater	All methods with exceptions noted within QAPP	Low	Defined below	Berney Kidd/CH2M HILL Peeyush Gupta/HTS

Personnel involved in data validation will be independent of any data generation effort. The Project Chemist will be responsible for overseeing data validation. Data validation will be carried out when the data packages are received from the laboratory. It will be performed on an analytical batch basis using the summary results of calibration and laboratory quality control, as well as those of the associated field samples. Data packages will be reviewed for all constituents of concern. Raw data will be reviewed for approximately 10 percent of the data packages or as deemed necessary by the Project Chemist. Validation will be performed using the following procedures and those referenced for Level 3 or 4 as appropriate:

- A review of the data set narrative to identify any issues that the lab reported in the data deliverable
- A check of sample integrity (sample collection, preservation, and holding times)
- An evaluation of basic QC measurements used to assess the accuracy, precision, and representativeness of data, including QC blanks, LCSs, MS/MSDs, surrogate recovery when applicable, and field or laboratory duplicate results
- A review of sample results, target compound lists, and detection limits to verify that project analytical requirements are met
- Initiation of corrective actions, as necessary, based on the data review findings
- Qualification of the data using appropriate qualifier flags, as necessary, to reflect data usability limitations

Level 3 validation procedures will also include reviewing the evaluation of calibration and quality control summary results against the project requirements and other method-specific QC requirements.

Data validation will be patterned after EPA guidelines for organic and inorganic data review, substituting the calibration and quality control requirements specified in this QAPP for those specified in the guidelines. The flagging criteria in Tables 36-2 and 36-3 will be used. The qualifier flags are defined in Table 36-4.

Qualifier flags, if required, will be applied to the electronic sample results. If multiple flags are required for a result, the most severe flag will be applied to the electronic result. The hierarchy of flags from the most severe to the least severe will be as follows: R, UJ, U, and J.

Any significant data quality problems will be brought to the attention of the Project Chemist.

TABLE 36-2
Flagging Conventions for Organic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Holding Time	Holding time exceed for extraction or analysis by less than a factor of two	J positive results UJ non-detects	affected samples
	Holding time exceed for extraction or analysis by a factor of two	J positive results R non-detects	affected samples
Temperature	temperature exceedance >6°C if received within 24 hr	UJ non-detects	affected samples
	temperature exceedance >6°C if received > 24 hr	UJ non-detects, J positive results	
Sample Preservation (volatiles)	Sample preservation requirements not met and analyzed out of holding time if preservation not performed in the field, but performed in the laboratory upon receipt, no flagging is required	J positive results R non-detects	affected samples
Sample Integrity (volatiles)	Professional Judgment on sample condition Example: Bubbles in VOA vial used for analysis	J positive results/professional judgment R non-detects/professional judgment	affected samples
GC/MS Instrument Performance Check	Mass assignment in error and laboratory cannot reprocess data	R all results	all samples in batch
	Ion abundance criteria not met	R all results if critical ions involved, use judgment otherwise	all samples in batch
Initial Calibration	%RSD > criteria in WS#28 or R <0.990	J positive results UJ non-detects	analyte in associated samples
	%RSD exceeds criteria by more than a factor of 2	J positive results R non-detects	analyte in associated samples
Continuing Calibration Verification (ICV and CCV)	% difference or % drift > criteria in WS#28	J positive results	analyte in associated samples
	% difference or % drift < criteria in WS#28	J positive results UJ non-detects	analyte in associated samples

TABLE 36-2
Flagging Conventions for Organic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (CLSD)	%R > criteria in WS#28	J positive results	analyte in associated samples
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	analyte in associated samples
	%R < criteria in WS#28 but <10%	J positive results R non-detects	analyte in associated samples
	RPD > criteria in WS#28	J positive results	analyte in associated samples
Method Blank	Multiply highest blank value by 5 (by 10 for common lab contaminants, acetone, methylene chloride, MIBK, cyclohexane, phthalates)	U positive results <5 x highest blank concentration (<10 x for common contaminants)	all associated samples in batch
Equipment Blank	Multiply highest blank value by 5 (by 10 for common lab contaminants, acetone, methylene chloride, MIBK, cyclohexane, phthalates)	U positive results <5 x highest blank concentration (<10 x for common contaminants)	all associated samples in batch
Trip Blank	Multiply highest blank value by 5 (by 10 for common lab contaminants, acetone, methylene chloride, MIBK, cyclohexane, phthalates)	U positive results <5 x highest blank concentration (<10 x for common contaminants)	all associated samples in batch
Matrix Spike/Matrix Spike Dup (MS/MSD) does not apply if sample result is greater than four times the spike value	%R > criteria in WS#28	J positive results	parent sample
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	parent sample
	%R < criteria in WS#28 but <10%	J positive results R non-detects	parent sample
	RPD > criteria in WS#28	J positive results	parent sample
Surrogates	%R > criteria in WS#28	J positive results	parent sample
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	parent sample
	%R < criteria in WS#28 but <10%	J positive results R non-detects	parent sample

TABLE 36-2
Flagging Conventions for Organic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Laboratory Duplicates	Both sample results >5 times RL and RPD>UCL	J positive results	laboratory duplicate pair
	One or both samples <5 times RL and a difference between results of ± 2 times RL	J positive results UJ non detects	laboratory duplicate pair
Field Duplicates	Both sample results >5 times RL and RPD>30%	J positive results	field duplicate pair
	One or both samples <5 times RL and a difference between results of ± 2 times RL	J positive results UJ non-detects	field duplicate pair

Initial calibration should be based on average response factors or a linear regression equation. Laboratories will need Project Chemist approval to use a nonlinear calibration curve.

TABLE 36-3
Flagging Conventions for Inorganic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Holding Time	Holding time exceeded for digestion or analysis	J positive results	affected samples
	Holding time exceeded for digestion or analysis by a factor of two	J positive results for all analytes R non-detects for all analytes	affected samples
Temperature (does not apply to SW6010C or SW6020)	temperature exceedance >6°C if received within 24 hr	UJ non-detects	affected samples
	temperature exceedance >6°C if received > 24 hr	UJ non-detects, J positive results	affected samples
Sample preservation	Sample preservation requirements not met. If preservation not performed in the field, but performed in the laboratory upon receipt, no flagging is required	J positive results for all analytes R non-detects for all analytes	affected samples
Initial Calibration	Correlation coefficient ≤0.995 or %RSD < criteria in WS#28	J positive results UJ non-detects	analyte in associated samples
Initial Calibration Verification (ICV)	%R > criteria in WS#28	J positive results	analyte in associated samples
	%R < criteria in WS#28	J positive results UJ non-detects	analyte in associated samples
Continuing Calibration Verification (CCV)	%R > criteria in WS#28	J positive results	analyte in associated samples
	%R < criteria in WS#28	J positive results UJ non-detects	analyte in associated samples
Interference Check Sample (metals only)	%R > criteria in WS#28	J positive results	analyte in associated samples
	%R < criteria in WS#28	J positive results UJ non-detects	analyte in associated samples
Laboratory Control Sample (LCS)/Laboratory Control Sample Duplicate (LCSD)	%R > criteria in WS#28	J positive results	analyte in associated samples
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	analyte in associated samples
	%R < criteria in WS#28 but <10%	J positive results R non-detects	analyte in associated samples

TABLE 36-3
Flagging Conventions for Inorganic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
	RPD > criteria in WS#28	J positive results	analyte in associated samples
Calibration Blank (ICB or CCB)	Multiply highest blank value by 5	U positive results < 5 x highest blank concentration	all associated samples in batch
	If negative blank and absolute value is greater than the MDL and negative value is >25% of sample result	J positive results UJ non-detects	analyte in associated samples
Method Blank	Multiply highest blank value by 5	U positive results < 5 x highest blank concentration	all associated samples in batch
	If negative blank and absolute value is greater than the MDL and negative value is >25% of sample result	J positive results UJ non-detects	analyte in associated samples
Equipment Blank	Multiply highest blank value by 5	U positive results < 5 x highest blank concentration	all associated samples in batch
Matrix Spike/Matrix Spike Dup (MS/MSD) does not apply if sample result is greater than four times the spike value	%R > criteria in WS#28	J positive results	parent sample
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	parent sample
	%R < criteria in WS#28 but <10%	J positive results R non-detects	parent sample
	RPD > criteria in WS#28	J positive results	parent sample
Serial Dilution (metals only)	If concentration is >50 times the MDL and % difference is > 10%	J positive results	parent sample
Post-Digestion Spike metals only perform if dilution test fails	%R > criteria in WS#28	J positive results	parent sample
	%R < criteria in WS#28 but ≥10%	J positive results UJ non-detects	parent sample
	%R < criteria in WS#28 but <10%	J positive results R non-detects	parent sample

TABLE 36-3
Flagging Conventions for Inorganic Methods
Quanta, Quality Assurance Project Plan

Quality Control Check	Evaluation	Flag	Samples Affected
Laboratory Duplicates (if no MSD or LCSD performed)	Both sample results >5 times RL and RPD>UCL	J positive results	parent sample
	One or both samples <5 times RL and a difference between results of ± 2 times RL	J positive results UJ non-detects	parent sample
Field Duplicates	Both sample results >5 times RL and RPD>30%	J positive results	field duplicate pair
	One or both samples <5 times RL and a difference between results of ± 2 times RL	J positive results UJ non-detects	field duplicate pair

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TABLE 36-4
Qualifier Flag Definitions
Quanta, Quality Assurance Project Plan

Flag	Definition
J	The result is an estimated quantity. The associated numerical value is the approximate concentration of the analyte in the sample.
R	The data are unusable. The sample results are rejected due to serious deficiencies in meeting Quality Control (QC) criteria. The analyte may or may not be present in the sample.
U	This analyte was analyzed for but not detected at the specified detection limit.
UJ	The analyte was analyzed for, but was not detected. The reported quantitation limit is approximate and may be inaccurate or imprecise.
NJ	The analysis indicates the presence of an analyte that has been “tentatively identified” and the associated numerical value represents its approximate concentration.

QAPP Worksheet #37: Data Usability Assessment

The data usability assessment is an evaluation based on the results of data verification and validation in the context of the overall project decisions or objectives. The assessment determines whether the project execution and resulting data meet the project DQOs. Both the sampling and analytical activities must be considered, with the ultimate goal of assessing whether the final, qualified results support the decisions to be made with the data.

All the results will be assembled and statistically reported for an overall Data Quality Evaluation (DQE), which will be provided as an appendix to the Remedial Design Report. The assessment report will identify precision and accuracy exceedances with respect to the laboratory performance for each batch of samples, as well as comparability of field and lab duplicates. Discussion will cover precision, accuracy, representativeness, comparability, and completeness as outlined in Worksheet #12. All data are usable for project decision-making unless rejected for project use.

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U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION II

GROUND WATER SAMPLING PROCEDURE
LOW STRESS (Low Flow) PURGING AND SAMPLING

I. SCOPE & APPLICATION

This Low Stress (or Low-Flow) Purging and Sampling Procedure is the EPA Region II standard method for collecting low stress (low flow) ground water samples from monitoring wells. Low stress Purging and Sampling results in collection of ground water samples from monitoring wells that are representative of ground water conditions in the geological formation. This is accomplished by minimizing stress on the geological formation and minimizing disturbance of sediment that has collected in the well. The procedure applies to monitoring wells that have an inner casing with a diameter of 2.0 inches or greater, and maximum screened intervals of ten feet unless multiple intervals are sampled. The procedure is appropriate for collection of ground water samples that will be analyzed for volatile and semi-volatile organic compounds (VOCs and SVOCs), pesticides, polychlorinated biphenyls (PCBs), metals, and microbiological and other contaminants in association with all EPA programs.

This procedure does not address the collection of light or dense non-aqueous phase liquids (LNAPL or DNAPL) samples, and should be used for aqueous samples only. For sampling NAPLs, the reader is referred to the following EPA publications: DNAPL Site Evaluation (Cohen & Mercer, 1993) and the RCRA Ground-Water Monitoring: Draft Technical Guidance (EPA/530-R-93-001), and references therein.

II. METHOD SUMMARY

The purpose of the low stress purging and sampling procedure is to collect ground water samples from monitoring wells that are representative of ground water conditions in the geological formation. This is accomplished by setting the intake velocity of the sampling pump to a flow rate that limits drawdown inside the well casing.

Sampling at the prescribed (low) flow rate has three primary benefits. First, it minimizes disturbance of sediment in the bottom of the well, thereby producing a sample with low turbidity (i.e., low concentration of suspended particles). Typically, this saves time and analytical costs by eliminating the need for collecting and analyzing an additional filtered sample from the same well. Second, this procedure

minimizes aeration of the ground water during sample collection, which improves the sample quality for VOC analysis. Third, in most cases the procedure significantly reduces the volume of ground water purged from a well and the costs associated with its proper treatment and disposal.

III. ADDRESSING POTENTIAL PROBLEMS

Problems that may be encountered using this technique include a) difficulty in sampling wells with insufficient yield; b) failure of one or more key indicator parameters to stabilize; c) cascading of water and/or formation of air bubbles in the tubing; and d) cross-contamination between wells.

Insufficient Yield

Wells with insufficient yield (i.e., low recharge rate of the well) may dewater during purging. Care should be taken to avoid loss of pressure in the tubing line due to dewatering of the well below the level of the pump's intake. Purging should be interrupted before the water level in the well drops below the top of the pump, as this may induce cascading of the sand pack. Pumping the well dry should therefore be avoided to the extent possible in all cases. Sampling should commence as soon as the volume in the well has recovered sufficiently to allow collection of samples. Alternatively, ground water samples may be obtained with techniques designed for the unsaturated zone, such as lysimeters.

Failure to Stabilize Key Indicator Parameters

If one or more key indicator parameters fails to stabilize after 4 hours, one of three options should be considered: a) continue purging in an attempt to achieve stabilization; b) discontinue purging, do not collect samples, and document attempts to reach stabilization in the log book; c) discontinue purging, collect samples, and document attempts to reach stabilization in the log book; or d) Secure the well, purge and collect samples the next day (preferred). The key indicator parameter for samples to be analyzed for VOCs is dissolved oxygen. The key indicator parameter for all other samples is turbidity.

Cascading

To prevent cascading and/or air bubble formation in the tubing, care should be taken to ensure that the flow rate is sufficient to maintain pump suction. Minimize the length and diameter of tubing (i.e., 1/4

or 3/8 inch ID) to ensure that the tubing remains filled with ground water during sampling.

Cross-Contamination

To prevent cross-contamination between wells, it is strongly recommended that dedicated, in-place pumps be used. As an alternative, the potential for cross-contamination can be reduced by performing the more thorough "daily" decontamination procedures between sampling of each well in addition to the start of each sampling day (see Section VII, below).

Equipment Failure

Adequate equipment should be on-hand so that equipment failures do not adversely impact sampling activities.

IV. PLANNING DOCUMENTATION AND EQUIPMENT

- Approved site-specific Field Sampling Plan/Quality Assurance Project Plan (QAPP). This plan must specify the type of pump and other equipment to be used. The QAPP must also specify the depth to which the pump intake should be lowered in each well. Generally, the target depth will correspond to the mid-point of the most permeable zone in the screened interval. Borehole geologic and geophysical logs can be used to help select the most permeable zone. However, in some cases, other criteria may be used to select the target depth for the pump intake. In all cases, the target depth must be approved by the EPA hydrogeologist or EPA project scientist.

- Well construction data, location map, field data from last sampling event.

- Polyethylene sheeting.

- Flame Ionization Detector (FID) and Photo Ionization Detector (PID).

- Adjustable rate, positive displacement ground water sampling pump (e.g., centrifugal or bladder pumps constructed of stainless steel or Teflon). A peristaltic pump may only be used for inorganic sample collection.

- Interface probe or equivalent device for determining the presence or absence of NAPL.

- Teflon or Teflon-lined polyethylene tubing to collect samples for organic analysis. Teflon or Teflon-lined polyethylene, PVC, Tygon or polyethylene tubing to collect samples for inorganic analysis. Sufficient tubing of the appropriate material must be available so that each well has dedicated tubing.

- Water level measuring device, minimum 0.01 foot accuracy, (electronic preferred for tracking water level drawdown during all pumping operations).

- Flow measurement supplies (e.g., graduated cylinder and stop watch or in-line flow meter).

- Power source (generator, nitrogen tank, etc.).
- Monitoring instruments for indicator parameters. Eh and dissolved oxygen must be monitored in-line using an instrument with a continuous readout display. Specific conductance, pH, and temperature may be monitored either in-line or using separate probes. A nephalometer is used to measure turbidity.

- Decontamination supplies (see Section VII, below).

- Logbook (see Section VIII, below).

- Sample bottles.

- Sample preservation supplies (as required by the analytical methods).

- Sample tags or labels, chain of custody.

V. SAMPLING PROCEDURES

Pre-Sampling Activities

1. Start at the well known or believed to have the least contaminated ground water and proceed systematically to the well with the most contaminated ground water. Check the well, the lock, and the locking cap for damage or evidence of tampering. Record observations.

2. Lay out sheet of polyethylene for placement of monitoring and sampling equipment.

3. Measure VOCs at the rim of the unopened well with a PID and FID instrument and record the reading in the field log book.

4. Remove well cap.

5. Measure VOCs at the rim of the opened well with a PID and an FID instrument and record the reading in the field log book.

6. If the well casing does not have a reference point (usually a V-cut or indelible mark in the well casing), make one. Note that the reference point should be surveyed for correction of ground water elevations to the mean geodesic datum (MSL).

7. Measure and record the depth to water (to 0.01 ft) in all wells to be sampled prior to purging. Care should be taken to minimize disturbance in the water column and dislodging of any particulate matter attached to the sides or settled at the bottom of the well.

8. If desired, measure and record the depth of any NAPLs using an interface probe. Care should be taken to minimize disturbance of any sediment that has accumulated at the bottom of the well. Record the observations in the log book. If LNAPLs and/or DNAPLs are detected, install the pump at this time, as described in step 9, below. Allow the well to sit for several days between the measurement or sampling of any DNAPLs and the low-stress purging and sampling of the ground water.

Sampling Procedures

9. Install Pump: Slowly lower the pump, safety cable, tubing and electrical lines into the well to the depth specified for that well in the EPA-approved QAPP or a depth otherwise approved by the EPA hydrogeologist or EPA project scientist. The pump intake must be kept at least two (2) feet above the bottom of the well to prevent disturbance and resuspension of any sediment or NAPL present in the bottom of the well. Record the depth to which the pump is lowered.

10. Measure Water Level: Before starting the pump, measure the water level again with the pump in the well. Leave the water level measuring device in the well.

11. Purge Well: Start pumping the well at 200 to 500 milliliters per minute (ml/min). The water level should be monitored approximately every five minutes. Ideally, a steady flow rate should be maintained that results in a stabilized water

level (drawdown of 0.3 ft or less). Pumping rates should, if needed, be reduced to the minimum capabilities of the pump to ensure stabilization of the water level. As noted above, care should be taken to maintain pump suction and to avoid entrainment of air in the tubing. Record each adjustment made to the pumping rate and the water level measured immediately after each adjustment.

12. Monitor Indicator Parameters: During purging of the well, monitor and record the field indicator parameters (turbidity, temperature, specific conductance, pH, Eh, and DO) approximately every five minutes. The well is considered stabilized and ready for sample collection when the indicator parameters have stabilized for three consecutive readings as follows (Puls and Barcelona, 1996):

    ±0.1 for pH
    ±3% for specific conductance (conductivity)
    ±10 mv for redox potential
    ±10% for DO and turbidity

    Dissolved oxygen and turbidity usually require the longest time to achieve stabilization. The pump must not be removed from the well between purging and sampling.

13. Collect Samples: Collect samples at a flow rate between 100 and 250 ml/min and such that drawdown of the water level within the well does not exceed the maximum allowable drawdown of 0.3 ft. VOC samples must be collected first and directly into sample containers. All sample containers should be filled with minimal turbulence by allowing the ground water to flow from the tubing gently down the inside of the container.

    Ground water samples to be analyzed for volatile organic compounds (VOCs) require pH adjustment. The appropriate EPA Program Guidance should be consulted to determine whether pH adjustment is necessary. If pH adjustment is necessary for VOC sample preservation, the amount of acid to be added to each sample vial prior to sampling should be determined, drop by drop, on a separate and equal volume of water (e.g., 40 ml). Ground water purged from the well prior to sampling can be used for this purpose.

14. Remove Pump and Tubing: After collection of the samples, the tubing, unless permanently installed, must be properly discarded or dedicated to the well for resampling by hanging the tubing inside the well.

15. Measure and record well depth.

16. Close and lock the well.

VI. FIELD QUALITY CONTROL SAMPLES

Quality control samples must be collected to determine if sample collection and handling procedures have adversely affected the quality of the ground water samples. The appropriate EPA Program Guidance should be consulted in preparing the field QC sample requirements of the site-specific QAPP.

All field quality control samples must be prepared exactly as regular investigation samples with regard to sample volume, containers, and preservation. The following quality control samples should be collected during the sampling event:

- Field duplicates
- Trip blanks for VOCs only
- Equipment blank (not necessary if equipment is dedicated to the well)

As noted above, ground water samples should be collected systematically from wells with the lowest level of contamination through to wells with highest level of contamination. The equipment blank should be collected after sampling from the most contaminated well.

VII. DECONTAMINATION

Non-disposable sampling equipment, including the pump and support cable and electrical wires which contact the sample, must be decontaminated thoroughly each day before use ("daily decon") and after each well is sampled ("between-well decon"). Dedicated, in-place pumps and tubing must be thoroughly decontaminated using "daily decon" procedures (see #17, below) prior to their initial use. For centrifugal pumps, it is strongly recommended that non-disposable sampling equipment, including the pump and support cable and electrical wires in contact with the sample, be decontaminated thoroughly each day before use ("daily decon").

EPA's field experience indicates that the life of centrifugal pumps may be extended by removing entrained grit. This also permits inspection and replacement of the cooling water in centrifugal pumps. All non-dedicated sampling equipment (pumps, tubing, etc.) must be

decontaminated after each well is sampled ("between-well decon," see #18 below).

17. **Daily Decon**

A) Pre-rinse: Operate pump in a deep basin containing 8 to 10 gallons of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

B) Wash: Operate pump in a deep basin containing 8 to 10 gallons of a non-phosphate detergent solution, such as Alconox, for 5 minutes and flush other equipment with fresh detergent solution for 5 minutes. Use the detergent sparingly.

C) Rinse: Operate pump in a deep basin of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

D) Disassemble pump.

E) Wash pump parts: Place the disassembled parts of the pump into a deep basin containing 8 to 10 gallons of non-phosphate detergent solution. Scrub all pump parts with a test tube brush.

F) Rinse pump parts with potable water.

G) Rinse the following pump parts with distilled/ deionized water: inlet screen, the shaft, the suction interconnector, the motor lead assembly, and the stator housing.

H) Place impeller assembly in a large glass beaker and rinse with 1% nitric acid (HNO_3).

I) Rinse impeller assembly with potable water.

J) Place impeller assembly in a large glass bleaker and rinse with isopropanol.

K) Rinse impeller assembly with distilled/deionized water.

18. **Between-Well Decon**

A) Pre-rinse: Operate pump in a deep basin containing 8 to 10 gallons of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.
B) Wash: Operate pump in a deep basin containing 8 to 10 gallons of a non-phosphate detergent solution, such as Alconox, for 5

minutes and flush other equipment with fresh detergent solution for 5 minutes. Use the detergent sparingly.

C) Rinse: Operate pump in a deep basin of potable water for 5 minutes and flush other equipment with potable water for 5 minutes.

D) Final Rinse: Operate pump in a deep basin of distilled/deionized water to pump out 1 to 2 gallons of this final rinse water.

VIII. FIELD LOG BOOK

A field log book must be kept each time ground water monitoring activities are conducted in the field. The field log book should document the following:

- Well identification number and physical condition.
- Well depth, and measurement technique.
- Static water level depth, date, time, and measurement technique.
- Presence and thickness of immiscible liquid layers and detection method.
- Collection method for immiscible liquid layers.
- Pumping rate, drawdown, indicator parameters values, and clock time, at three to five minute intervals; calculate or measure total volume pumped.
- Well sampling sequence and time of sample collection.
- Types of sample bottles used and sample identification numbers.
- Preservatives used.
- Parameters requested for analysis.
- Field observations of sampling event.
- Name of sample collector(s).
- Weather conditions.
- QA/QC data for field instruments.

IX. REFERENCES

Cohen, R.M. and J.W. Mercer, 1993, DNAPL Site Evaluation, C.K. Smoley Press, Boca Raton, Florida.

Puls, R.W. and M.J. Barcelona, 1996, Low-Flow (Minimal Drawdown) Ground-water Sampling Procedures, EPA/540/S-95/504.

U.S. EPA, 1993, RCRA Ground-Water Monitoring: Draft Technical Guidance, EPA/530-R-93-001.

U.S. EPA Region II, 1989, CERCLA Quality Assurance Manual.

Monitoring Well Sediment Sampling
January 20, 2014
Kyle Block/CH2M HILL

APPROVED:

_____	1/20/2014 _____ Date
_____	1/20/2014 _____ Date
_____	1/20/2014 _____ Date

Annual Review Summary

Annual Reviewer				
Date of Review				

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Attachments

Attachment 1 – Equipment List

A. Purpose and Applicability

The purpose of this Standard Operating Procedure (SOP) is to establish uniform procedures for collection of sediment that has accumulated within monitoring wells for mineralogical evaluation at the Quanta Resources Corporation Superfund Site.

B. Summary of Method

The sediment sample will be collected by placing peristaltic pump tubing on the bottom of the well and the sediment and water (presumed to be suspended to some degree in the groundwater) will be pumped out, passed through a field filter to allow the accumulation of the sediment on the filter surface. The sample will be collected so that anoxic conditions are maintained, to the extent practicable. Sediment will be removed from the filter, placed in a bag and shipped.

C. Definitions

AHA Activity Hazard Analysis

FSP Field Sampling Plan

FTL Field Team Leader

HANDS health and safety database

OSHA Occupational Safety and Health Administration

SSC Site Safety Coordinator

USEPA United States Environmental Protection Agency

D. Health and Safety

CH2M HILL staff will have current Occupational Safety and Health Administration (OSHA) and 8-hour OSHA refresher training, as applicable. Staff will review and sign the site health and safety plan (HASP), will review and sign the activity hazard analysis (AHA) for the task, and understand and use personal protective equipment as specified in the HASP.

E. Personnel Qualifications

This SOP is written for CH2M HILL staff. The Field Team Leader (FTL) will be responsible for the execution of the Work Plan. The FTL will be identified by the Project Manager before the start of the task. The site safety coordinator (SSC) will have completed the CH2M HILL-required SSC training, and will be responsible for the execution of the HASP. All CH2M Hill staff will have current OSHA and 8-hour OSHA refresher training, as applicable. The SSC will verify that all HASP-required training using the HANDS database and any lapsed training is updated before the start of the task, and that copies of training for each staff member are onsite.

F. Equipment and Supplies

Attachment 1 contains equipment and supplies for sampling

The following equipment will be needed:

- Water level meter

- Chain-of-custody forms
- Shipping labels and forms
- Ice
- Bubble wrap and packing material
- Lab bottles and coolers
- Field sample forms
- Field book
- Indelible ink pens and sharpies
- 55-gallon drum
- Peristaltic Pump
- Teflon tubing (preferably 3/8 to ½ inch diameter)
- Phosphate-free detergent (such as Alconox) and spray bottles, buckets, brushes, and plastic sheeting required for decontamination
- Camera for digital photographs
- Re-sealable plastic bags
- Air monitoring equipment (per HASP and FSP) with calibration regulators and calibration gas
- PPE per the HASP and FSP
- 5-gallon buckets with lids
- Hand-pump vacuum filtration kit (hand pump, tubing, filters) [http://www.rickly.com/sai/filtrationequip.htm#Hand-Held Vacuum/Pressure Pumps]
    - Range of filter sizes will likely be needed, attempt 0.45 micron first, but also have larger filter sizes available if this size is not practical.
- Cooler with dry ice

G. Procedural Steps

The following section outlines collection and sampling techniques to be used during the investigation:

- Preparation:
    - The bottom of a large sample cooler, preferably 23” x 14” x 14” (WxLxH) or larger, is covered with dry ice and approximately 500mL of water. The lid to the cooler should remain closed until samples are ready to be collected.
    - Filtration equipment should be prepared ahead of time, to the extent possible.
- Sample Collection (this will likely require two people):
    - Measure depth to water and depth to bottom upon opening the well.
    - A peristaltic pump with relatively large diameter tubing (e.g., 3/8 to ½ inch) should be used to maximize sediment recovery, if possible. The field team should be prepared with standard sized

tubing and pump heads in case the larger diameter tubing doesn't produce enough suction to sample the well.

- One sampler will lower the sampling hose to a depth corresponding to the mid-point of the well screen. The well does not need to be fully purged, but 2 to 3 hose volumes should be moved through the tubing in order to prime the tubing and minimize the amount of oxygen sorbed to the hose surface. The recovered groundwater should be containerized at the surface and disposed of in accordance with the site IDW procedures.
- The second sampler will prep the filtration vessel and then submerge it into the air space of the anoxic handling vessel inverting it SLOWLY five times. At this point, the filtration vessel must never leave the confines of the anoxic handling vessel until the entire sampling procedure is complete.
- Lower the intake end of the tubing to the bottom of the well and pump the groundwater-sediment slurry into the filtration cup that is kept within the confines of the cooler. The pump tubing should discharge to the filtration vessel within the anoxic chamber. Approximately 5 to 10 grams of sediment will be needed for the required analyses; however, the field team should collect as much as can be reasonably recovered.
    - Samples should be filtered using the smallest mesh size possible. Ideally, a 0.45 micron filter would be used; however, this may not be practicable depending on the sediment type.
        - Within the confines of the cooler the filters/sediment are then place in a zip-top bag, the air expelled, and the bag sealed. Samples are stored on ice and in the dark.
    - If the samples cannot be readily filtered, a second option is to collect the samples into 40 mL vials with zero head space and send to the lab. The recommended procedure for this is:
        - place the end of the tubing near the bottom of the vial
        - fill vial until it overflows with sediment
        - while overflowing, slowly pull the tubing out of the vial and quickly place the cap on top, so there is no headspace.
        - At least 2-3 vials should be collected per well in order to obtain sufficient volume.
        - Samples should be stored on ice and in the dark (i.e., cooler)
        - Glass containers other than 40 mL vials could be used as long as the lids are air-tight.
- During sampling, the sediment color, grain size, and odor will be noted.
- The lid on the dry ice cooler should be closed when not in use to minimize carbon dioxide loss.

H. Data and Records Management

Observations and data will be recorded on a field form or the field book. Additional information such as field photographs and instrument calibration will be documented on a field form, boring log, or field book. Field data will be finalized the day of collection. Hardcopy records will be scanned and copied to a project directory at least weekly. Electronic records will be backed up on a laptop or similar device daily, and will be copied to a project directory at least weekly.

Chain-of-custody (COC) forms will be completed and accompany soil samples to the specified laboratory.

I. Quality Assurance and Quality Control

Follow and document procedures noted above and in accordance with quality assurance/quality control (QA/QC) procedures specified in the UFP-QAPP for the HCAA.

Equipment Decontamination
July 16, 2012
Erik Spande/CH2M HILL

APPROVED:

_____ 7/16/2012
Author Date

_____ 7/16/2012
Date

_____ 7/16/2012
Date

Annual Review Summary

Annual Reviewer	Erik Spande			
Date of Review	6/7/2013			

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Attachments

Attachment 1 – Equipment List

A. Purpose and Applicability

The purpose of this Standard Operating Procedure (SOP) is to establish uniform procedures for equipment decontamination. The procedures outlined in this SOP are applicable the decontamination of heavy equipment, drilling equipment, well materials, and sampling equipment.

B. Summary of Method

Decontamination procedures were established in Section 3.2 of the Field Sampling Plan by Parsons (2005), and these instructions are summarized in this SOP.

C. Definitions

AHA Activity Hazard Analysis

FSP Field Sampling Plan

FTL Field Team Leader

HandS health and safety database

OSHA Occupational Safety and Health Administration

SSC Site Safety Coordinator

USEPA United States Environmental Protection Agency

D. Health and Safety

CH2M HILL staff will have current Occupational Safety and Health Administration (OSHA) and 8-hour OSHA refresher training, as applicable. Staff will review and sign the site health and safety plan (HASP), will review and sign the activity hazard analysis (AHA) for the task, and understand and use personal protective equipment as specified in the HASP.

E. Personnel Qualifications

This SOP is written for CH2M HILL staff. The field team leader (FTL) will be responsible for the execution of the Work Plan and Field Sampling Plan. The FTL will be identified by the Project Manager before the start of the task. The site safety coordinator (SSC) will have completed the CH2M HILL-required SSC training and will be responsible for the execution of the HASP. All CH2M HILL staff will have current OSHA and 8-hour OSHA refresher training, as applicable. The SSC will verify that all HASP-required training using the HandS database and any lapsed training is updated before the start of the task, and that copies of training for each staff member are onsite.

F. Equipment and Supplies

Attachment 1 contains equipment and supplies for decontamination activities.

G. Procedural Steps

Decontamination Pad for Drilling Equipment or Other Heavy Equipment

- The location of the decontamination pad will be determined in the field.

- The drilling or heavy equipment subcontractor will construct a decontamination pad of high-density polyethylene sheeting.
- The pad will be sloped such that water drains toward a sump, and the sides of the decontamination pad will be bermed to contain decontamination water.
- Water from the sump will be pumped to a 55-gallon drum.

Heavy Equipment Decontamination

- The subcontractor will use a high-pressure steam-cleaning unit for decontamination of drill rigs, augers, bits, rods, tools, split-spoon samplers, and tremie pipes before work and after the conclusion of each boring.
- Wire brushes will be used to remove dirt, grease, and oil as needed.
- Tools, drill rods, and augers will be placed on sawhorses or polyethylene plastic sheets following steam cleaning. Direct contact with the ground will be prevented.
- Well material such as well casings and screens will be decontaminated as heavy equipment unless they arrive at the site in factory-sealed plastic sleeves.

Sampling Equipment Decontamination

- Dedicated and disposable equipment will not need to be decontaminated. All sampling equipment that will be reused will be decontaminated using these procedures. Sampling equipment such as split spoons may be steam-cleaned (see Heavy Equipment Decontamination) or may be decontaminated by using the procedure noted below.
- Clean disposable equipment (groundwater sampling tubing, bladders for pumps, sampling spoons, etc.) should be used when necessary to minimize cross-contamination. Disposable equipment does not have to be decontaminated.
- Conduct sampling equipment decontamination at the decontamination pad. If the pad is not present, then sampling equipment decontamination will occur within buckets that are placed on plastic sheeting.
- Wash sampling equipment such as low-flow pumps, bowls, spoons, augers, Geoprobe rods, and Macrocore samplers with potable water and then phosphate-free detergent (such as Alconox).
- Equipment will undergo a acid rinse consisting of a 10 percent solution of reagent grade nitric acid and deionized water if sampling for metals.
- Rinse with potable water and then rinse with distilled water.
- Between rinses, place equipment on plastic sheeting or aluminum foil, as needed.
- Decontaminated equipment will be wrapped in aluminum foil for storage or transportation from the decontamination area to the sampling area. Decontaminated equipment will not be placed on the ground.

H. Data and Records Management

Record the time and procedures used for decontamination in the field book or field form. Field data will be finalized the day of collection. Hardcopy records will be scanned and copied to a project directory at least weekly. Electronic records will be backed up on a laptop or similar device daily, and will be copied to a project directory at least weekly.

I. Quality Assurance and Quality Control

Follow and document procedures noted above and in accordance with quality assurance/quality control (QA/QC) procedures specified in the QAPP, as previously amended (CH2M HILL, 2005, 2006, 2008), and in the current QAPP Addendum (CH2M HILL, 2012).

J. References

CH2M HILL. 2005. Quality Assurance Project Plan (Revised), Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey. October.

CH2M HILL. 2006. Quality Assurance Project Plan (Revised), Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey. November.

CH2M HILL. 2008. Quality Assurance Project Plan (Revised), Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey. November.

CH2M HILL. 2012a. Draft Predesign Investigation Work Plan, Quanta Resources Corporation Superfund Site, Operable Unit 1, Edgewater, New Jersey. May.

CH2M HILL. 2012b. Field Sampling Plan for Predesign Investigation, Operable Unit 1, Quanta Resources OU1, Edgewater, New Jersey. May.

Parsons. 2005. *Field Sampling Plan, Operable Unit 1, Quanta Resources OU1,* Edgewater, New Jersey. May.

K. Attachments/Checklists

1. Equipment Checklist

Attachment 1 – Equipment List

Heavy equipment and well material decontamination equipment will be supplied by the drilling subcontractor.

- Plastic-lined decontamination pad of high density polyethylene sheeting—sides of decon pad will be bermed
- Sump for decontamination pad
- High-pressure steam cleaning unit
- Sawhorses
- Polyethylene plastic sheets
- 55-gallon drums for decon water

Decontamination Equipment for Sampling Equipment and PPE

- Alconox® solution (or equivalent)
- Potable water
- Deionized water
- Diluted reagent grade acid (Nitric Acid)
- Spray bottles for alconox solution, diluted acid, potable water, and distilled water. Each type of spray bottle used for decontamination will be labeled.
- Brushes
- 5-gallon buckets with lids
- Four or more 5-gallon buckets for decontamination of pumps
- Aluminum foil
- Protective gloves (nitrile or latex, per HASP)

Alkalinity

DOC316.53.01166

Phenolphthalein and Total Alkalinity

Method 8203

10 to 4000 mg/L as $CaCO_3$

Digital Titrator

Scope and Application: For water, wastewater and seawater.

Test preparation

Before starting the test:

Four drops of Bromcresol Green-Methyl Red Indicator Solution[1] can be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow.
Four drops of Phenolphthalein Indicator Solution[1] can be substituted for the Phenolphthalein Indicator Powder Pillow.
For added convenience when stirring, use the TitraStir® stirring apparatus[1].
meq/L Alkalinity = mg/L as $CaCO_3$ ÷ 50

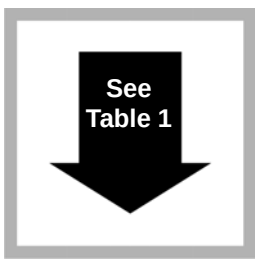
[1] See *Optional reagents and apparatus*.

Collect the following items:

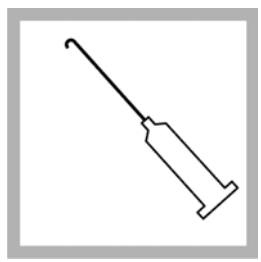
Description	Quantity
Bromcresol Green-Methyl Red Indicator Powder Pillow	1 pillow
Phenolphthalein Indicator Powder Pillow	1 pillow
Sulfuric acid titration cartridge (see *Range-specific information*)	1 cartridge
Digital titrator	1
Delivery tube for digital titrator	1
Graduated cylinder	1
Erlenmeyer flask, 250-mL	1

See *Consumables and replacement items* for reorder information.

Alkalinity

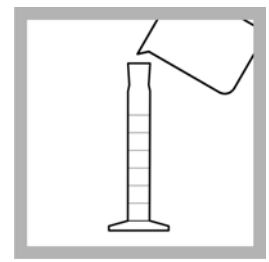


1. Select a sample volume and titration cartridge from the *Range-specific information* table.



2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator.

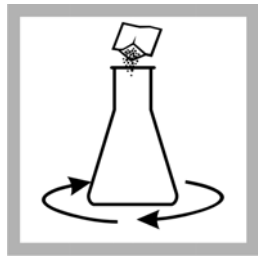
3. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and wipe the tip.



4. Use a graduated cylinder or pipet to measure the sample volume from the *Range-specific information* table.

Alkalinity (continued)

5. Transfer the sample into a clean, 250-mL Erlenmeyer flask. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



6. Add the contents of one Phenolphthalein Indicator Powder Pillow. Swirl to mix.

If the solution turns pink, proceed to step 7. If the solution is colorless, the Phenolphthalein (P) alkalinity is zero. Proceed to step 9.

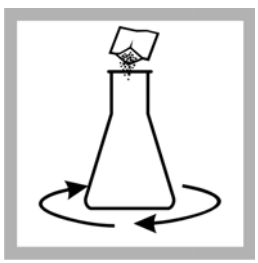
7. Place the delivery tube into the solution and swirl the flask. Turn the knob on the titrator to add titrant to the solution. Continue to swirl the flask and add titrant until the color changes from pink to colorless.

Write down the number of digits displayed on the counter.

8. Use the multiplier in the *Range-specific information* table to calculate the concentration:

digits x multiplier = mg/L as $CaCO_3$ P alkalinity

Example: 100 mL of sample was titrated with the 0.1600 N cartridge and 250 digits were used to reach the endpoint. The concentration is 250 x 0.1 = 25 mg/L as $CaCO_3$



9. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow. Swirl to mix.

10. Continue the titration with sulfuric acid to a light pink color.

Write down the number of digits displayed on the counter.

Note: A pH meter may be used to titrate to a specific pH as required by sample composition. See the *End point pH* table.

11. Use the multiplier in the *Range-specific information* table to calculate the concentration:

digits x multiplier = mg/L as $CaCO_3$ total alkalinity

Example: 100 mL of sample was titrated with the 0.1600 N cartridge and 250 digits were used to reach the endpoint. The concentration is 250 x 0.1 = 25 mg/L as $CaCO_3$

Table 29 Range-specific information

Range (mg/L as $CaCO_3$)	Sample volume (mL)	Titration cartridge (N H_2SO_4)	Multiplier
10–40	100	0.1600	0.1
40–160	25	0.1600	0.4
100–400	100	1.600	1.0
200–800	50	1.600	2.0
500–2000	20	1.600	5.0
1000–4000	10	1.600	10.0

Table 30 End point pH

Sample composition	Total alkalinity	Phenolphthalein alkalinity
Alkalinity about 30 mg/L	pH 4.9	pH 8.3
Alkalinity about 150 mg/L	pH 4.6	pH 8.3
Alkalinity about 500 mg/L	pH 4.3	pH 8.3
Silicates or phosphates present	pH 4.5	pH 8.3
Industrial wastes or complex system	pH 4.5	pH 8.3
Routine or Automated Analyses	pH 4.5	pH 8.3

Interferences

Interfering substances lists substances that can interfere with this test.

Table 31 Interfering substances

Interfering substance	Interference level
Chlorine	Chlorine at levels above 3.5 mg/L may cause a yellow-brown color when the Bromcresol Green-Methyl Red Powder Pillow is added. Add one drop of 0.1 N Sodium Thiosulfate to the sample to remove chlorine before starting the test.
Color or turbidity	Color or turbidity can mask the color change of the end point. Use a pH meter instead of the color indicators and titrate to a pH of 8.3 for phenolphthalein acidity. For total alkalinity see *End point pH* for the correct end point pH.

Sample collection, preservation and storage

- Collect samples in clean plastic or glass bottles. Fill completely and cap tightly.
- Prevent excessive agitation or prolonged exposure to air. Complete the test procedure as soon as possible after collection for best accuracy.
- The sample can be stored for at least 24 hours if cooled to 4 °C (39 °F) or below.
- Warm to room temperature before the test is started.

Alkalinity relationship table

Total alkalinity primarily includes hydroxide, carbonate and bicarbonate alkalinities. The concentration of these alkalinities in a sample may be determined when the phenolphthalein and total alkalinities are known (see *Alkalinity relationships*).

To use the table follow these steps:

g. Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.

h. Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.

i. Divide the total alkalinity by 2 to give one-half the total alkalinity.

j. Select Row 3, 4 or 5 based on comparing the result of step c (one-half total alkalinity) with the total alkalinity.

k. Perform the required calculations in the appropriate row, if any.

l. Check your results. The sum of the three alkalinity types will equal the phenolphthalein alkalinity.

For example:
A sample has 170 mg/L as $CaCO_3$ phenolphthalein alkalinity and 250 mg/L as $CaCO_3$ total alkalinity. What is the concentration of hydroxide, carbonate and bicarbonate alkalinities?

The phenolphthalein alkalinity does not equal 0 (it is 170 mg/L), see step g.

The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L), see step h.

One-half of the total alkalinity (250 g/L) equals 125 mg/L. Because the phenolphthalein alkalinity (170 mg/L) is greater than one-half the total alkalinity (125 mg/L), select row 5.

The hydroxide alkalinity is equal to:
2 x 170 = 340

340 – 250 = 90 mg/L hydroxide alkalinity

The carbonate alkalinity is equal to:
250 – 170 = 80

80 x 2 = 160 mg/L carbonate alkalinity

The bicarbonate alkalinity equals 0 mg/L.
Check: (See step l)

90 mg/L hydroxide alkalinity + 160 mg/L carbonate alkalinity + 0 mg/L bicarbonate alkalinity = 250 mg/L

The above answer is correct; the sum of each type equals the total alkalinity.

Table 32 Alkalinity relationships

Row	Sample result	Hydroxide alkalinity equals:	Carbonate alkalinity equals:	Bicarbonate alkalinity equals:
1	Phenolphthalein Alkalinity = 0	0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one-half of Total Alkalinity	0	Phenolphthalein Alkalinity times 2	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one-half of Total Alkalinity	0	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one-half of Total Alkalinity	2 times Phenolphthalein Alkalinity minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

Accuracy check

End point confirmation
Use a buffer pillow with the same pH as the end point with the indicator to make sure the end point color is accurate.

- Phenolphthalein alkalinity—Add 50 mL of deionized water to a flask. Add one pH 8.3 buffer powder pillow and one Phenolphthalein Indicator Powder Pillow and swirl to mix. Use this solution for comparison during the titration with the sample.
- Total alkalinity—Add 50 mL of deionized water to a flask. Add one pH 4.5 buffer powder pillow and one Bromcresol Green-Methyl Red Indicator Powder Pillow and swirl to mix. Use this solution for comparison during the titration with the sample.

Standard additions method (sample spike)
Required for accuracy check:

- Alkalinity Voluette® Ampule Standard Solution, 0.500 N
- Ampule breaker
- TenSette Pipet, 0.1–1.0 mL and Pipet Tips

1. Open the standard solution ampule.
2. Use the TenSette Pipet to add 0.1 mL of the standard to the titrated sample. Swirl to mix.
3. Titrate the spiked sample to the end point. Write down the amount of titrant that was used to reach the end point.
4. Repeat steps 2 and 3, using two more additions of 0.1 mL. Titrate to the end point after each addition.
5. Each 0.1 mL of standard that was added will use approximately 25 digits of the 1.600 N titration cartridge or 250 digits of the 0.1600 N titration cartridge to reach the endpoint. If more or less titrant was used, there may be an interference (see *Interferences*) or the concentration of the titrant has changed.

Summary of method

The sample is titrated with sulfuric acid to a colorimetric end point corresponding to a specific pH. Phenolphthalein alkalinity is determined by titration to a pH of 8.3, as evidenced by the color change of phenolphthalein indicator and indicates the total hydroxide and one half the carbonate present. M (methyl orange) or T (total) alkalinity is determined by titration to a pH between 4.3 and 4.9 and includes all carbonate, bicarbonate and hydroxide. Alternatively, total alkalinity end points may be determined by using a pH meter and titrating to the specific pH required for the sample composition.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Alkalinity Reagent Set (approximately 100 tests)			2271900
(1) Bromcresol Green-Methyl Red Powder Pillows	1 pillow	100/pkg	94399
(1) Phenolphthalein Indicator Powder Pillows	1 pillow	100/pkg	94299
(1) Sulfuric Acid Titration Cartridge, 0.1600 N	varies	each	1438801
(1) Sulfuric Acid Titration Cartridge, 1.600 N	varies	each	1438901

Required apparatus

Description	Quantity/Test	Unit	Catalog number
Digital Titrator		each	1690001
Flask, Erlenmeyer, graduated, 250-mL	1	each	50546
Graduated cylinder—select one or more based on range:			
Cylinder, graduated, 10-mL	1	each	50838
Cylinder, graduated, 25-mL	1	each	50840
Cylinder, graduated, 50-mL	1	each	50841
Cylinder, graduated, 100-mL	1	each	50842

Recommended standards

Description	Unit	Catalog number
Alkalinity Standard Solution, Voluette® Ampule 0.500 N Na_2CO_3, 10-mL	16/pkg	1427810

Optional reagents and apparatus

Description	Unit	Catalog number
Buffer Powder Pillows, pH 4.5	25/pkg	89568
Buffer Powder Pillows, pH 8.3	25/pkg	89868
Stir bar, octagonal 28.6 mm x 7.9 mm	each	2095352
TenSette Pipet, 0.1 to 1.0 mL	each	1970001
Water, deionized	500 mL	27249
Pipet, volumetric, Class A, 10 mL	each	1451538
Pipet, volumetric, Class A, 20 mL	each	1451520
Pipet Filler, safety bulb	each	1465100
Bottles, sampling, poly, 500 mL	each	2087079
Bromphenol Green-Methyl Red indicator solution	100 mL MDB	2329232
Phenolphthalein Indicator solution, 5 g/L	100 mL MDB	16232
pH meter	each	—
TitraStir stir plate, 115 Vac	each	1940000
TitraStir stir plate, 230 Vac	each	1940010

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Bacteria, Sulfate-reducing

DOC316.53.01326

Visual determination

SRB-BART™*

Semi-quantitative

Scope and Application: For the determination of sulfate-reducing bacteria in brine solutions, produced waters and hydraulic fracturing waters.

*SRB-BART is a trademark of Droycon Bioconcepts Inc.

Test preparation

Procedure notes:

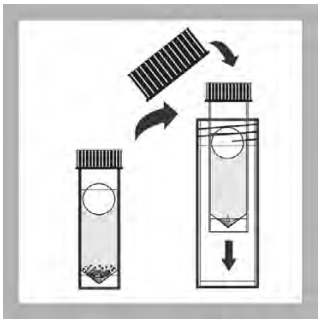
Do not touch or contaminate the inside of the tube or lid. Use aseptic technique.
To prevent contamination when the cap is removed from the inner tube, set the cap down directly on a clean surface. Do not invert the cap.
Do not shake or swirl the tube after the sample is added. Let the ball float to the top at its own speed.
SRB grow predominantly deep within biofilms and not directly in water. Make sure to get a representative sample.

Test procedure

1. Remove the inner tube from the outer tube.

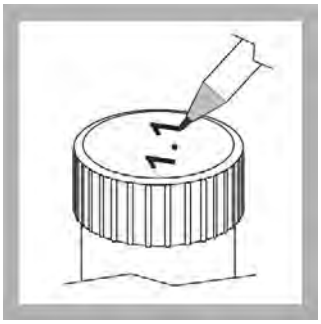
2. Collect at least 20 mL of sample in the outer tube.

3. Fill the inner tube with the sample to the fill line. Tighten the cap on the inner tube.



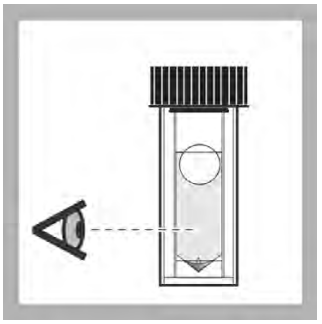
4. Put the inner tube in the outer tube and tighten the cap on the outer tube.

Do not shake or swirl the tube!



5. Write the date and sample name on the outer tube.

6. Incubate the tube at room temperature and away from direct sunlight. Do not move the tube.



7. Examine the tube each day for 8 days. Record the date when a reaction is first seen. Refer to *Test results*.

Interferences

If the sample contains more than 20 ppm hydrogen sulfide (H_2S), the test can give a false positive. To remove hydrogen gas from the sample, add 30 mL of sample to the outer tube, cap and shake for 10 seconds. Let stand for 20 seconds.

Test results

Presence/Absence

When sulfate-reducing bacteria are present, a black slime forms in the tube. Refer to Figure 1.

Figure 1 Negative versus positive test results

Negative (absent/non-aggressive) **Positive (present/aggressive)**

Make an estimate of the bacteria population

If the test result is positive, make an estimate of the bacteria population and the aggressivity. Refer to Table 1. A faster reaction occurs when the bacteria population is high.

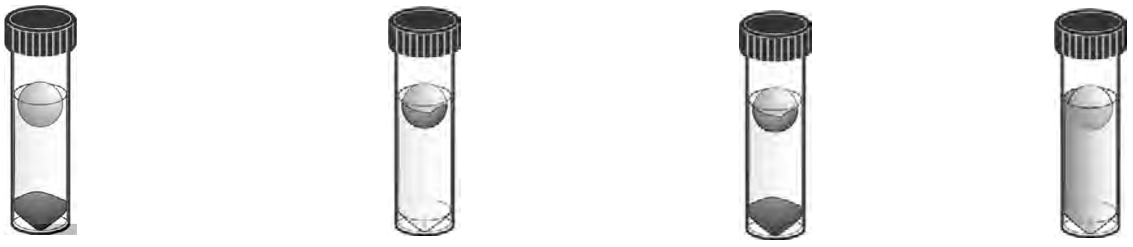
Table 1 Approximate bacteria population

Days to reaction	Approximate slime population (cfu/mL)	Aggressivity
1	6,800,000	Very high
2	700,000	High
3	100,000	High
4	18,000	Moderate
5	5000	Moderate
6	1200	Moderate
7	500	Moderate
8	200	Low

Advanced test information

If the test result is positive, examine the tubes for dominant bacteria. Refer to Figure 2.

Figure 2 Dominant bacteria



Black in the bottom only—dense anaerobic bacteria dominated by Desulfovibrio

Black around the ball only—aerobic SRB with aerobic slime forming heterotrophs

Black in the bottom and around the ball—aerobic and anaerobic SRB

Cloudy solution—anaerobic bacteria

Summary of method

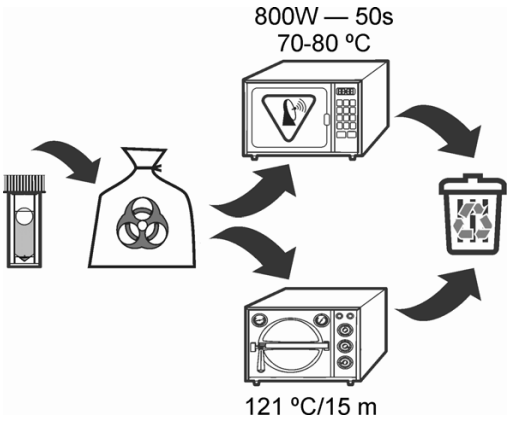
When sulfate-reducing bacteria are in the sample, sulfate is reduced to hydrogen sulfide (H_2S) in the SRB-BART vial during incubation. The H_2S reacts with the ferrous iron in the test vial to form black iron sulfides. This sulfide commonly forms either in the base as a black precipitate and/or around the ball as an irregular black ring.

SRB tend to grow in anaerobic conditions deep within biofilms (slimes) as a part of a microbial community. SRB may not be present in the free-flowing water over the site of the fouling. Sulfate-reducing bacteria can cause problems such as strong odors, blackening of equipment, slime formations and the start of corrosive processes.

Disposal

Sterilize the reacted sample before disposal. Refer to Figure 3.

Figure 3 Disposal



Consumables and replacement items

Required reagents and apparatus

Description	Quantity/Test	Unit	Item no.
BART Test for sulfate-reducing bacteria	1	9/pkg	2432409
BART Test for sulfate-reducing bacteria	1	27/pkg	2432427

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07/2013, Edition 2

26672-88

• Iron, Ferrous, Test Kit

1,10 Phenanthroline Iron Reagent Method

• Trousse d'analyse fer ferreux

Méthode réactif fer 1, 10 Phéanthroline

• Eisen, 2wertig Test Kit

1,10 Phenanthrolin-Eisenreagenz Methode

• Kit de análisis para hierro ferroso

Método reactivo de fenatrolina de hierro 1,10

0.0 – 10.0 mg/L

• Mod. IR-18C

• # 26672-00

- To ensure accurate results, read carefully before proceeding.
- Pour obtenir des résultats exacts, lire attentivement le mode d'emploi avant d'utiliser la trousse.
- Um genaue Ergebnisse zu gewährleisten, lesen Sie das Folgende bitte aufmerksam durch, bevor Sie fortfahren.
- Para obtener resultados precisos, lea detenidamente las instrucciones antes de proceder al análisis.

WARNING

Handling chemical samples, standards, and reagents can be dangerous. Review the Material Safety Data Sheets before handling any chemicals.

ATTENTION

La manipulation des échantillons chimiques, étalons et réactifs peut être dangereuse. Lire les fiches de données de sécurité des produits avant de manipuler tout produit chimique.

WARNUNG

Die Handhabung chemischer Proben, Standards und Reagenzien kann gefährlich sein. Bitte gehen Sie die Materialsicherheitsdatenblätter durch, bevor Sie Chemikalien handhaben.

ADVERTENCIA

El manejo de sustancias químicas, patrones y reactivos, puede resultar peligroso. Lea las fichas de informaciones de seguridad de materiales antes de manipular cualquier producto químico.

HACH®

Introduction

The 1,10 phenanthroline indicator in the Ferrous Iron Reagent reacts with ferrous iron in the sample to form an orange color in proportion to the ferrous iron concentration. Ferric iron does not react. The ferric iron (Fe^{3+}) concentration can be determined by subtracting the ferrous iron concentration from the results of a total iron test.

Introduction

L'indicateur 1,10 phénanthroline dans le réactif fer ferreux réagit avec le fer ferreux présent dans l'échantillon pour former une coloration orange proportionnelle à la concentration de fer ferreux. Le fer ferrique ne réagit pas. La concentration de fer ferrique (Fe^{3+}) peut être déterminée en soustrayant la concentration de fer ferreux des résultats d'une analyse de fer total.

Einleitung

Der 1,10 Phenantrolin Indikator im Eisen(II)-Reagenz reagiert mit Eisen(II) in der Probe durch Bildungen einer orangen Farbe, proprotional zur Konzentration des zweiwertigen Eisens. Eisen(III) reagiert nicht. Die Konzentration des dreiwertigen Eisen (Fe^{3+}) kann bestimmt werden, indem man die Konzentration des zweiwertigen Eisens von den Ergebnissen eines Eisen Gesamt Tests subtrahiert.

Introducción

El indicador de 1,10-fenantrolina en el Reactivo para Hierro Ferroso reacciona con el hierro ferroso de la muestra para formar un color anaranjado en proporción con la concentración de hierro ferroso. El hierro férrico no reacciona. La concentración de hierro férrico (Fe^{3+}) puede ser determinada restando la concentración de hierro ferroso de el resultado de una prueba de hierro total.

Measuring Hints and General Test Information

- Wash all labware between tests. Contamination may alter test results. Clean with a non-abrasive detergent or a solvent such as isopropyl alcohol. Use a soft cloth for wiping or drying. Do not use paper towels or tissue on plastic tubes as this may scratch them. Rinse with clean water (preferably deionized water).
- Rinse all viewing tubes thoroughly with the sample water before testing.
- Use clippers to open plastic powder pillows.
- For critical testing, reagent accuracy should be checked with each new lot of reagents. Prepare a ferrous iron stock solution (100 mg/L Fe) by dissolving 0.702 grams of ferrous ammonium sulfate, hexahydrate, in one liter deionized water. Dilute 5.00 mL of this solution to 100 mL with deionized water to make a 5.0 mg/L standard solution. Prepare this immediately before use. Follow the ferrous iron test instructions using this solution instead of a water sample.

Conseils pour les mesures et informations générales sur l’analyse

- Laver toute la verrerie entre les analyses. La contamination peut fausser les résultats d’analyses. Laver avec un détergent non abrasif ou un solvant tel que l’isopropanol. Utiliser un tissu doux pour essuyer ou sécher. Ne pas utiliser de tissu ou papier d’essuyage sur les tubes en plastique pour ne pas les rayer. Rincer à l’eau propre (de préférence de l’eau désionisée).
- Rincer soigneusement tous les tubes colorimétriques avec l’échantillon d’eau avant l’analyse.
- Utiliser la pince coupante pour ouvrir les gélules en plastique.
- Pour des analyses critiques, l’exactitude du réactif doit être vérifiée pour chaque nouveau lot de réactifs. Préparer une solution-mère de fer ferreux (100 mg/L Fe) en dissolvant 0,702 grammes d’ammonium-fer (II) sulfate, hexahydrate, dans un litre d’eau désionisée. Diluer 3,00 mL de cette solution à 100 mL avec de l’eau désionisée pour obtenir une solution étalon à 3,0 mg/L. Préparer cette solution immédiatement avant emploi. Suivre les instructions d’analyse du fer ferreux en remplaçant l’échantillon par cette solution étalon.

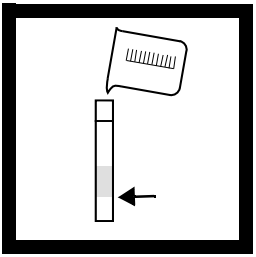
Meßtips und allgemeine Testinformationen

- Waschen Sie alle Laborartikel zwischen den Tests. Verunreinigung kann die Testergebnisse verfälschen. Reinigen Sie sie mit einem nicht scharfen Detergent oder einem Lösungsmittel wie zum Beispiel Isopropylalkohol. Verwenden Sie für das Abwischen oder Abtrocknen ein weiches Tuch. Verwenden Sie bei den Plastikröhrchen keine Papierhandtücher oder Tissue-Papier, da dieses sie zerkratzen kann. Spülen Sie mit sauberem Wasser (vorzugsweise entsalztes Wasser).
- Spülen Sie alle Prüfröhrchen vor dem Test gründlich mit dem Probenwasser.
- Verwenden Sie eine Schere zur Öffnung der Plastik-Pulverkissen.
- Um genaue Bestimungen zu erzielen, sollte die Genauigkeit der Reagenzien für jede neue Charge überprüft werden. Bereiten Sie eine Eisen-II Stammlösung (100mg/L Fe) auf, indem Sie 0,702 Gramm Eisen-II Ammoniumsulfat, hexahydrat, in einem Liter entsalzten Wasser lösen. 3,00 mL dieser Lösung werden mit 100 mL entsalztem Wasser verdünnt, so dass eine 3,0 mg/L Standardlösung entsteht. Diese Lösung wird unmittelbar vor Gebrauch angesetzt. Arbeiten Sie, unter Benutzung dieser Lösung anstelle einer Wasserprobe, gemäß den Anweisungen für den Eisen(II) Test.

Consejos para la medición e información general sobre el análisis

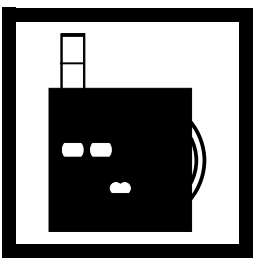
- Lavar todo el material de laboratorio entre los análisis. La contaminación puede alterar los resultados. Limpiar con un detergente no abrasivo o con un solvente como el alcohol isopropílico. Utilizar un paño suave para limpiar o secar. No utilizar ni toallitas ni pañuelos de papel para limpiar los tubos de plastico para no rayarlos. Aclarar con agua limpia (preferentemente agua desionizada).
- Enjuagar todos los tubos para colorimetría abundantemente con la muestra de agua antes de realizar el análisis.
- Utilice las pinzas cortantes para abrir las cápsulas de plástico.
- Para pruebas exigentes o difficiles, la precisión del reactivo debe ser verificada cada vez que se comienza con un nuevo lote. Preparar una solución de reserva de hierro ferroso (100 mg/L Fe), disolviendo 0,702 gs. de sulfato de amonio ferroso, hexahidrato, en un litro de agua desionizada. Diluya 3,00 mL de esta solución en 100 mL de agua desionizada para hacer una solución estándar de 3,00 mg/L. Esta debe ser preparada inmediatamente antes de usarla. Siga las instrucciones de la prueba de hierro ferroso empleando esta solución en vez de una muestra de agua.

• Procedure • Technique • Verfahren • Procedimiento



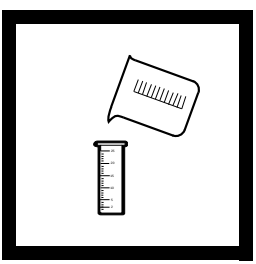
1. Fill a viewing tube to the first (5-mL) line with sample water. This is the blank.

- ♦ Remplir un tube colorimétrique jusqu'au premier trait (5 mL) avec l'échantillon d'eau. Ceci est le blanc.
- ♦ Füllen Sie ein Prüfröhrchen bis zur ersten (5 mL) Linie mit Probenwasser. Dieses ist die Blindprobe.
- ♦ Llene un tubo para colorimetría hasta la primera marca (5 mL) con la muestra de agua. Esto constituye el blanco.



2. Place this tube in the top left opening of the color comparator.

- ♦ Placer ce tube dans l'ouverture supérieure gauche du comparateur.
- ♦ Stellen Sie dieses Röhrchen in die obere linke Öffnung des Farbkomparators.
- ♦ Coloque este tubo en la abertura superior izquierda del comparador.

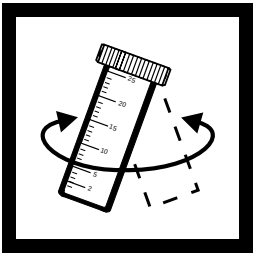


3. Fill the measuring vial to the 25-mL mark with sample water.

- ♦ Remplir le tube de mesure jusqu'au trait 25 mL avec l'échantillon d'eau.
- ♦ Füllen Sie das Messröhrchen bis zur 25 mL Markierung mit dem Probenwasser.
- ♦ Llene el frasco medidor hasta la marca de 25 mL con el agua de la muestra.

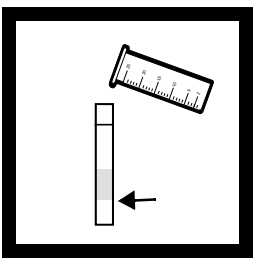
4. Add the contents of one Ferrous Iron Reagent Powder Pillow to the measuring vial.

- ♦ Ajouter le contenu d'une gélule de réactif du fer ferreux au tube de mesure.
- ♦ Geben Sie den Inhalt eines Eisen(II)-Reagenz-Pulverkissens in das Messröhrchen.
- ♦ Agregue el contenido de una cápsula del Reactivo para Hierro Ferroso al frasco medidor.



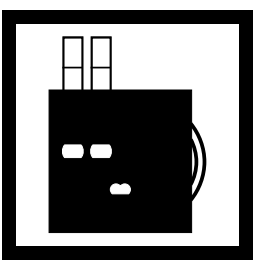
5. Swirl to mix. An orange color will develop if ferrous iron is present. Allow three minutes for full color development.

- ♦ Agiter pour mélanger. En présence de fer ferreux, une coloration orange se développe. Attendre le développement complet de la coloration.
- ♦ Schwenken Sie zum Vermischen. Ist Eisen(II) vorhanden, entwickelt sich eine orange Färbung. Warten Sie drei Minuten, bis sich die Farbe vollständig ausgebildet hat.
- ♦ Agite para mezclar. Se formará un color anaranjado en presencia de hierro ferroso. Deje pasar tres minutos para que el color se desarrolle completamente.



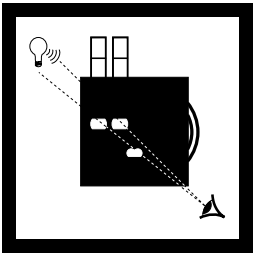
6. Fill another viewing tube to the first (5-mL) mark with the prepared sample.

- ♦ Remplir un autre tube jusqu'au premier trait (5 mL) avec l'échantillon préparé.
- ♦ Füllen Sie ein weiteres Prüfröhrchen bis zur ersten (5 mL-) Linie mit der vorbereiteten Probe.
- ♦ Llene otro tubo para colorimetría hasta la marca de 5mL con la muestra preparada en los puntos 4 y 5.



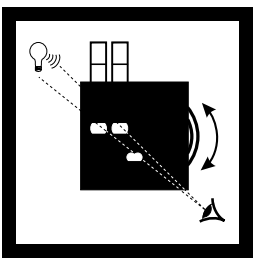
7. Place the second tube in the top right opening of the color comparator.

- ♦ Placer le second tube dans l'ouverture supérieure droite du comparateur.
- ♦ Setzen Sie das zweite Röhrchen in die obere rechte Öffnung des Farbkomparators.
- ♦ Coloque el segundo tubo en la abertura superior derecha del comparador.



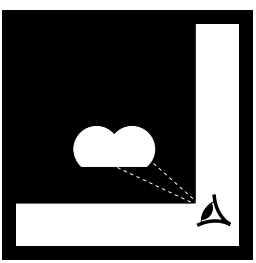
8. Hold comparator up to a light source such as the sky, a window or a lamp. Look through the openings in front.

- ♦ Tenir le comparateur face à une surface uniformément éclairée (ciel, lampe, fenêtre) et regarder par les ouvertures de la face antérieure du comparateur.
- ♦ Halten Sie den Komparator gegen eine Lichtquelle wie zum Beispiel den Himmel, ein Fenster oder eine Lampe. Sehen Sie durch die Öffnungen vorn.
- ♦ Lleve el comparador hasta una fuente de luz, tal como el cielo, una ventana o una lámpara. Mire a través de las aberturas frontales del comparador.



9. Rotate the color disc until the color matches in the two openings.

- ♦ Tourner le disque jusqu'à égalité des teintes dans les deux ouvertures.
- ♦ Drehen Sie die Farbscheibe, bis die Farbe in den beiden Öffnungen übereinstimmt.
- ♦ Haga girar el disco de color hasta que el color coincida en ambas aberturas.



10. Read the mg/L ferrous iron in the scale window.

- ♦ Lire la concentration du fer ferreux en mg/L dans la fenêtre de l'échelle.
- ♦ Lesen Sie die mg/L Eisen(II) im Skalenfenster ab.
- ♦ Lea la concentración de hierro ferroso en mg/L en la ventanilla graduada.

REPLACEMENTS

Description	Unit	Cat. No.
Clippers	each	968-00
Color Comparator	each	1732-00
Color Disc, Iron Phenanthroline	each	1874-00
Ferrous Iron Reagent Powder Pillows, 25 mL	100/pkg	1037-69
Instruction Card, IR-18C Test Kit	each	26672-88
Vial, measuring, with 2, 5, 10, 15, 20 and 25-mL marks	each	2193-00
Viewing Tube, plastic	4/pkg	46600-04
Water, deionized	4 L	272-56

REACTIFS ET PIECES DE RECHANGE

Désignation	Unité	Réf. Nº
Pince coupante pour gélules moyennes	1	968-00
Comparateur	1	1732-00
Disque coloré fer, phénanthroline	1	1874-00
Réactif du fer ferreux en gélules pour 25 mL	100/paq	1037-69
Mode d'emploi de la trousse IR-18C	1	26672-88
Tube de mesure marqué 2, 5, 10, 15, 20 et 25 mL	1	2193-00
Tube colorimétrique en plastique avec bouchon	4/paq	46600-04
Eau désionisée	4 L	272-56

VERBRAUCHSMATERIAL UND ERSATZTEILE

Beschreibung	Einheit	Kat. Nr.
Abschneider	1	968-00
Farbkomparator	1	1732-00
Farbscheibe, Eisenphenanthrolin	1	1874-00
Eisen(II) Reagenz-Pulverkissen, 25 mL	100/Stck	1037-69
Anleitungskarte, IR-18C Test Kit	1	26672-88
Messröhrchen m. 2, 5, 10, 15, 20 und 25 mL Markierungen	1	2193-00
Farbprüfröhrchen, Plastik, mit Kappe	4/Stck	46600-04
Entsalztes Wasser	4 L	272-56

REACTIVOS Y MATERIALES

Descripción	Unidad	Nº Ref.
Pinzas cortantes para cápsulas intermedias	1	968-00
Comparador de Colores	1	1732-00
Disco de colores, fenantrolina de hierro	1	1874-00
Reactivo para Hierro Ferroso, Bolsas de Polvo, 25 mL	100/lote	1037-69
Tarjeta de Instrucciones, Juego de Prueba IR-18C	1	26672-88
Frasco medidor, con marcas a 2, 5, 10, 15, 20 y 25 mL	1	2193-00
Tubo para colorimetría de plástico, con tapa protectora	4/lote	46600-04
Agua desionizada	4 L	272-56

OPTIONAL REAGENTS AND EQUIPMENT

Description	Unit	Cat. No.
Caps, for plastic Color Viewing Tubes 46600-04	4/pkg	46600-14
Ferrous Ammonium Sulfate, Hexahydrate	113 g	11256-14
Flask, volumetric, Class A, 100-mL	each	26366-42
Flask, volumetric, Class A, 1000-mL	each	26366-53
Pipet, volumetric, Class A, 5-mL	each	14515-37
Pipet Filler, safety bulb	each	14651-00

REACTIFS ET EQUIPEMENTS OPTIONNELS

Désignation	Unité	Réf. Nº
Bouchons pour tubes en plastique 46600-04	4/paq	46600-14
Ammonium, fer (II) sulfate, 6 H_2O ACS	113 g	11256-14
Fiole jaugée, classe A, 100ml	1	26366-42
Fiole jaugée, classe A, 1000 ml	1	26366-53
Pipette jaugée, classe A, 5,00ml	1	14515-37
Poire à pipetter	1	14651-00

ZUSÄTZLICHE REAGENZIEN UND ZUBEHÖR

Beschreibung	Einheit	Kat. Nr.
Kappen, für Plastik-Farbprüfröhrchen 46600-04	4/Stck	46600-14
Eisen(II)-Ammoniumsulfat, hexahydrat	113 g	11256-14
Messkolben, Klasse A, 100 mL	1	26366-42
Messkolben, Klasse A, 1000 mL	1	26366-53
Messpipette, Klasse A, 5mL	1	14515-37
Pipettenfüller, Sicherheitsball	1	14651-00

REACTIVOS Y EQUIPAMIENTO OPCIONALES

Descripción	Unidad	Nº Ref.
Tapas protectoras para tubos de plástico 46600-04	4/lote	46600-14
Sulfato de Amonio Ferroso, Hexahidratado	113 g	11256-14
Frasco volumétrico, clase A, 100-mL	1	26366-42
Frasco volumétrico, clase A, 1000-mL	1	26366-53
Pipeta volumétrica, clase A, 5-0 mL	1	14515-37
Bulbo de seguridad para llenador de pipeta.	1	14651-00

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Sulfide

DOC316.53.01136

USEPA[1] Methylene Blue Method[2] **Method 8131**

5 to 800 µg/L S^{2-} (spectrophotometers) **Reagent Solution**

0.01 to 0.70 mg/L (colorimeters)

Scope and application: For testing total sulfides, H_2S, HS^-, and certain metal sulfides in groundwater, wastewater, brines and seawater.

[1] USEPA approved for reporting wastewater analysis. Procedure is equivalent to Standard Method 4500-S2– D.
[2] Adapted from Standard Methods for the Examination of Water and Wastewater.

Test preparation

Instrument specific information

The table in this section shows all of the instruments that have the program for this test. Table 1 shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests.

To use the table, select an instrument, then read across to find the corresponding information for this test.

Table 1 Instrument-specific information for reagent addition

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700	The fill line is to the right.	2495402
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
Some sulfide loss can occur if dilution is necessary.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used and use any recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Use the Safety Data Sheets for disposal information for unused reagents. Consult the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

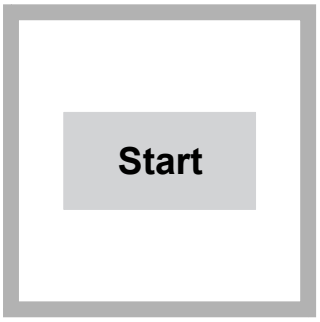
Description	Quantity
Sulfide 1 Reagent	1–2 mL
Sulfide 2 Reagent	1–2 mL
Water, deionized	10–25 mL
Pipet, serological, 10-mL	1
Pipet Filler, safety bulb	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument specific information on page 1.)	2
Stoppers	2

Refer to Consumables and replacement items on page 5 for reorder information.

Sample collection

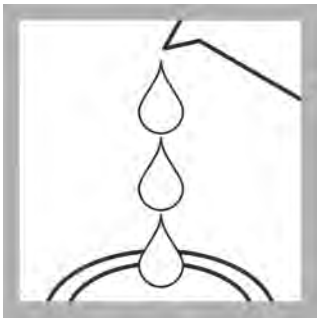
- Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles with tight-fitting caps. Fill the bottle completely and immediately tighten the cap.
- Prevent agitation of the sample or exposure to air.

Methylene Blue Method

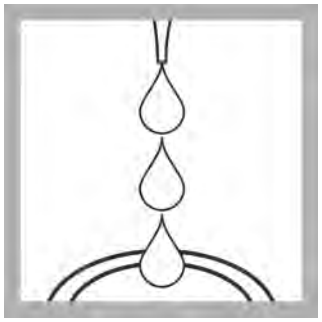


1. Start program **690 Sulfide**. For information about sample cells, adapters or light shields, refer to Instrument specific information on page 1.

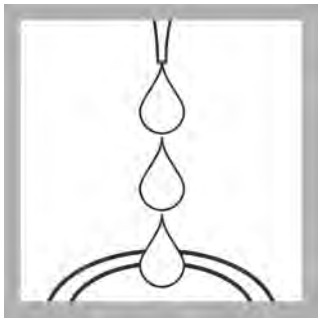
Note: *Although the program name may vary between instruments, the program number does not change.*



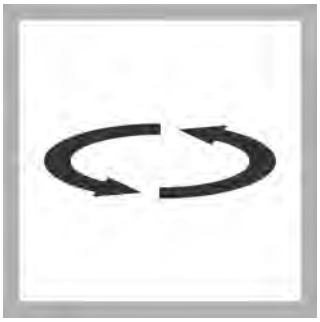
2. Prepare the blank: Fill a sample cell with deionized water. Use 10 mL for spectrophotometers and 25 mL for colorimeters.



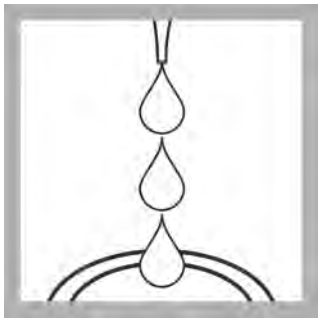
3. Prepare the sample: Use a pipet to add sample to a second sample cell. Use 10 mL for spectrophotometers and 25 mL for colorimeters. Do not mix the sample more than necessary to prevent sulfide loss.



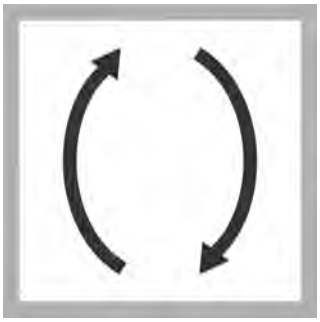
4. Use a dropper to add 0.5 mL Sulfide 1 Reagent to each cell.



5. Swirl to mix.

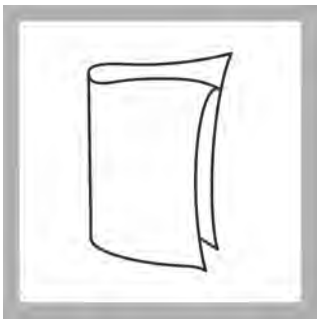


6. Use the dropper to add Sulfide 2 Reagent to each cell. Use 0.5 mL for spectrophotometers and 1.0 mL for colorimeters.



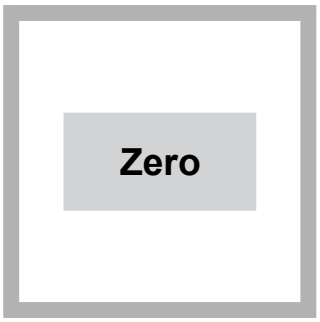
7. Close the sample cell. Invert the sample cell to mix. A pink color will develop initially. If sulfide is present, the solution becomes blue.

8. Start the instrument timer. A five-minute reaction time starts.

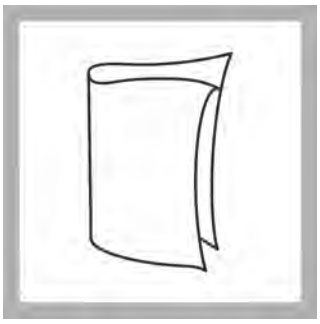


9. When the timer expires, clean the blank.

10. Insert the blank into the cell holder.



11. Push **ZERO**. The display shows 0 µg/L or 0.00 mg/L S^{2-}.



12. Clean the prepared sample.

13. Insert the prepared sample into the cell holder.

14. Push **READ**. Results show in µg/L or mg/L S^{2-}.

Soluble sulfides

To measure soluble sulfides, use a centrifuge to separate the solids. To make an estimate of the amount of insoluble sulfides in the sample, subtract the soluble sulfide concentration from the total (with solids) sulfide concentration.

1. Fill a centrifuge tube completely with sample and immediately cap the tube.
2. Put the tube in a centrifuge and run the centrifuge to separate the solids.
3. Use the supernatent as the sample in the test procedure.

Interferences

Interfering substance	Interference level
Barium	Concentrations more than 20 mg/L react with the sulfuric acid in Sulfide 1 Reagent and form a $BaSO_4$ (barite) precipitate. To correct for this interference: **1.** Dilute the sample in the test procedure as follows: • Spectrophotometers: use a 0.1-mL or 1.0-mL sample volume and add deionized water to the 10-mL mark. • Colorimeters: use a 0.25-mL or 2.5-mL sample volume and add deionized water to the 25-mL mark. **2.** Let the sample fully react with both reagents. **3.** After the 5 minute reaction period, pour the sample into a 50-mL beaker. **4.** Pull the sample into a Luer-Lock syringe (10 cc for spectrophotometers; 60 cc for colorimeters). **5.** Put a 0.45-µm filter disc on the Luer-Lock tip and filter the sample into a clean sample cell for measurement. Use deionized water to prepare the blank.
Strong reducing substances such as sulfite, thiosulfate and hydrosulfite	Prevent the full color development or reduce the blue color
Sulfide, high levels	High concentrations of sulfide can inhibit the full color development. Use a diluted sample in the test procedure. Some sulfide loss can occur when the sample is diluted.
Turbidity	Pre-treat the sample to remove sulfide, then use the pre-treated sample as the blank in the test procedure. Prepare a sulfide-free blank as follows: **1.** Measure 25 mL of sample into a 50-mL Erlenmeyer flask. **2.** Add 30-g/L Bromine Water by drops with constant swirling until a yellow color remains. **3.** Add 30-g/L Phenol Solution by drops with constant swirling until the yellow color is removed. **4.** Use this solution to replace the deionized water blank in the test procedure.

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users may get different results under different test conditions.

Program	Standard	Precision (95% Confidence Interval)	Sensitivity Concentration change per 0.010 Abs change
690	520 µg/L S^{2-}	504–536 µg/L S^{2-}	5 µg/L S^{2-}

Summary of method

Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. High sulfide levels in oil field waters may be determined after proper dilution. The measurement wavelength is 665 nm for spectrophotometers or 610 nm for colorimeters.

Pollution prevention and waste management

Reacted samples contain hexavalent chromium and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Water, deionized	varies	4 L	27256
Sulfide Reagent Set	—	—	2244500
Includes:			
Sulfide 1 Reagent	1–2 mL	100 mL MDB	181632
Sulfide 2 Reagent	1 –2 mL	100 mL MDB	181732

Required apparatus

Description	Quantity/test	Unit	Item no.
Pipet, serological, graduated, 10-mL	1	each	53238
Pipet filler, safety bulb	1	each	1465100
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Optional reagents and apparatus

Description	Unit	Item no.
Bromine Water, 30-g/L	29 mL	221120
Phenol Solution, 30-g/L	29 mL	211220
Stoppers for 18-mm tube	25/pkg	173125
Flask, Erlenmeyer, 50 mL	each	50541

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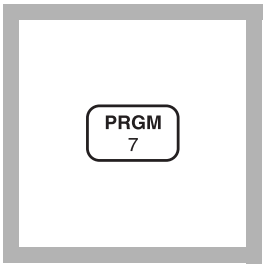
04/2013, Edition 8

SULFIDE (0 to 0.70 mg/L S^{2-})

For water, wastewater and seawater

Methylene Blue Method* USEPA accepted for reporting wastewater analysis**

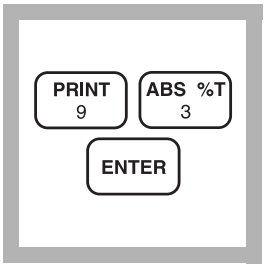


1. Enter the stored program number for sulfide (S).

Press: **PRGM**

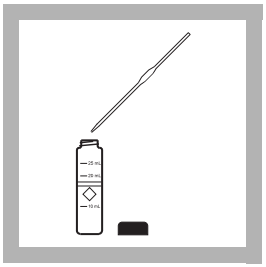
The display will show:

PRGM ?



2. Press: **93 ENTER**

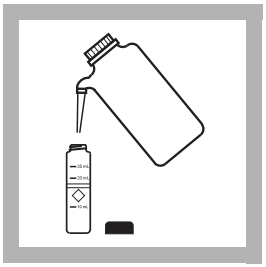
The display will show **mg/L, S** and the **ZERO** icon**.**



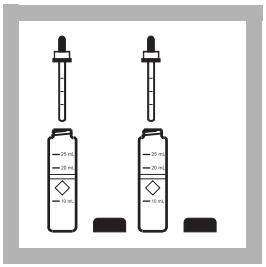
3. Pipet 25 mL of sample into a clean sample cell. This will be the prepared sample.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis. Use a pipet to avoid agitation.*

Note: *For field testing, a 25-mL graduated cylinder may be used.*

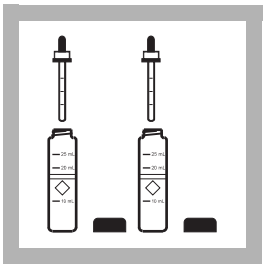


4. Fill a second sample cell with 25 mL of deionized water (the blank).



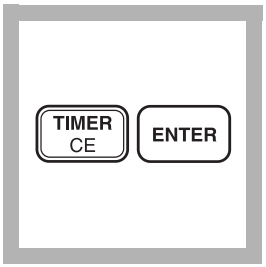
5. Add 1.0 mL of Sulfide 1 Reagent to each cell. Swirl to mix.

Note: *Use the calibrated 1-mL dropper.*



6. Add 1.0 mL of Sulfide 2 Reagent to each cell. Immediately swirl to mix.

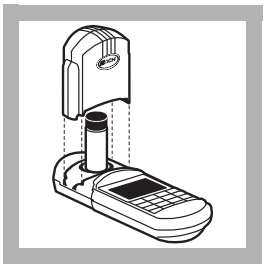
Note: *A pink color will develop, then the solution will turn blue if sulfide is present.*



7. Press:

TIMER ENTER

A 5-minute reaction period will begin.



8. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

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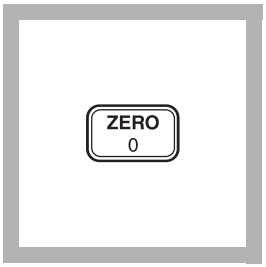
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

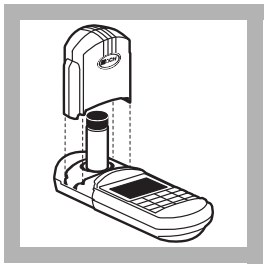
** Procedure is equivalent to USEPA method 376.2 or Standard Method 4500-S^{2-} D for wastewater.



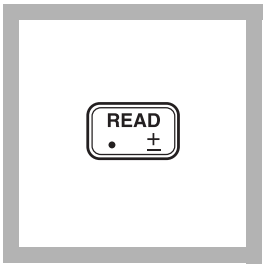
9. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L S



10. After the timer beeps, place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L sulfide will be displayed.

Note: *Some sulfide loss may occur if dilution is necessary.*

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples immediately.

Accuracy Check

Sulfide standards are unstable and must be user prepared. See Sandard Methods, 4500S^{-} for preparation and standardization directions.

Method Performance

Precision

In a single laboratory, using standard solutions of 0.73 mg/L sulfide and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ± 0.02 mg/L sulfide.

Estimated Detection Limit (EDL)

The EDL for program 93 is 0.01 mg/L S^{2-}. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Strong reducing substances (sulfite, thiosulfate and hydrosulfite)	Interfere by reducing the blue color or preventing its development.
Sulfide, high levels	High concentrations of sulfide may inhibit full color development and require sample dilution. Some sulfide loss may occur when the sample is diluted.
Turbidity	For turbid samples, prepare a sulfide-free blank as follows. Use it in place of the deionized water blank in the procedure. **1.** Measure 25 mL of sample into a 50-mL erlenmeyer flask. **2.** Add Bromine Water dropwise with constant swirling until a permanent yellow color just appears. **3.** Add Phenol Solution dropwise until the yellow color just disappears. Use this solution in Step 4 in place of deionized water.

Soluble Sulfides

Determine soluble sulfides by centrifuging the sample in completely filled, capped tubes and analyzing the supernatant. Insoluble sulfides are then estimated by subtracting the soluble sulfide concentration from the total sulfide result.

Summary of Method

Hydrogen sulfide and acid-soluble metal sulfides react with N, N-dimethyl-p-phenylenediamine oxalate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. High sulfide levels in oil field waters may be determined after dilution.

Pollution Prevention and Waste Management

Sulfide 2 Reagent contains potassium dichromate. The final solution will contain hexavalent chromium (D007) at a concentration regulated as a hazardous waste by Federal RCRA. See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS

	Cat. No.
Sulfide Reagent Set (100 tests)	22445-00
Includes: (2) 1816-42, (2) 1817-42	

Description	Quantity Required Per Test	Units	Cat. No.
Sulfide 1 Reagent	2 mL	100 mL MDB	1816-32
Sulfide 2 Reagent	2 mL	100 mL MDB	1817-32
Water, deionized	25 mL	4 L	272-56

REQUIRED APPARATUS

Cylinder, graduated, 25 mL	1	each	508-40
Pipet, volumetric, Class A, 25.00 mL	1	each	14515-40
Pipet Filler, safety bulb	1	each	14651-00
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Description	Units	Cat. No.
Bromine Water, 30 g/L	29 mL	2211-20
Phenol Solution, 30 g/L	29 mL	2112-20
Sodium Sulfide, hydrate	114 g	785-14

OPTIONAL APPARATUS

Bottle, Wash, 250 mL	each	620-31
Dropper, for 1 oz. bottle	each	2258-00
Flask, erlenmeyer, 50 mL	each	505-41
Standard Methods for the Examination of Water and Wastewater	each	22708-00

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ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager _____

QA Manager _____

Effective Date: 4/26/11

TITLE: TOTAL SEMI-VOLATILE PETROLEUM HYDROCARBONS

METHOD REFERENCE: SW846 Method 8015B (12/96)

Revised Sections: **2.1, 3.1, 6.1.1, 8.2, 10.1.1, 10.2.1, 10.3.1, 12.6.3, 13.6.1, 13.7.1**

SCOPE AND APPLICATION

1.1 This method is based on a solvent extraction and gas chromatographic procedure utilizing a flame ionization detector (FID). The method may be utilized to detect hydrocarbons in the Diesel Range Organics (DRO), where the C_8 to C_{44} hydrocarbon range corresponds to a boiling point range between approximately 170 °C and 430 °C. However, the routine reporting range is C_{10} to C_{28}.

1.2 The method is suitable for the analysis of the extracts prepared from all types of solid waste matrices, soils, and water samples.

1.0 SUMMARY

2.1 The sample is extracted with methylene chloride and concentrated in a KD apparatus. The extract is analyzed by capillary GC column equipped with a flame ionization detector(FID.) The chromatogram may be integrated within the C_8 to C_{44} range, or client specified range, and quantified with a calibration factor.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve(100 µg/ml for waters and 10 mg/kg for soils).

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. See individual types of Blanks: Method Blank; Instrument Blank, Storage Blank, and Sulfur Blank.

BLANKSPIKE - a blank matrix (reagent water or clean sand) is spiked with the targeted parameters and analyzed using the same method used for samples. Accuracy data is compared to laboratory derived limits to determine if the method is in control.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours to verify the initial calibration of the system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the terms continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the flame ionization detector to the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is <u>not</u> synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards, which is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - as used in this SOP and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 °C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

REAGENT WATER - water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest.

RELATIVE PERCENT DIFFERENCE (RPD) - as used in this SOP and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the instrument response of an analyte. Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RETENTION TIME (RT) – the time required (in minutes) for a standard compound to elute from a chromatographic column.

INSTRUMENT BLANK – a system evaluation sample containing lab reagent grade water with internal standards and surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses.

5.3 Primary standards of toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 COLLECTION, PRESERVATION AND HOLDING TIME

6.1 Collection & Preservation

6.1.1 Aqueous samples are collected in 1 liter glass bottle with Teflon lined cap. Samples must be preserved with 5 ml of 50% HCl at the time of collection (acid must be added to the bottle prior to adding the sample).

6.1.2 Soil samples are collected in 300-ml amber jars with Teflon lined cap.

6.1.3 The samples must be protected from light and refrigerated at 0 to ≤6°C from the time of receipt until extraction and analysis.

6.1.4 Sample extracts are stored at 0 to ≤6°C, protected from light.

6.2 Holding Time

6.2.1 Aqueous sample must be extracted within 7 days of sampling.

6.2.2 Soil sample must be extracted within 14 days of sampling.

6.2.3 All extracts must be analyzed within 40 days following extraction.

7.0 APPARATUS AND MATERIALS

7.1 Microsyringes - 10 ul, 25 ul, 100 ul, 500 ul, and 1000 ul.

7.2 Volumetric flasks - 10 ml, 50 ml, 100 ml.

7.3 Disposable pasteur pipets.

7.4 10 ul graduated syringe, manually held (Hamilton or equiv.).

7.5 10 ul graduated syringe, auto sampler (Hamilton or equiv.).

7.6 Gas Chromatograph, equipped with a flame ionization detector, capable of temperature programming.

7.7 Autosampler

7.8 GC column - 30m x 0.25mm ID, DB-5, 0.5u film or equivalent.

7.9 Data Integrator - Data system capable of summing peaks, re-analyzing data files after revising integration parameters, and manually drawing chromatographic baselines as necessary. The ENVIROQUANT (PC) data system is capable of quantitation using multi-point calibration.

8.0 STANDARDS & REAGENTS

8.1 Solvents - Ultra pure, chromatography grade methylene chloride.

8.2 Diesel stock standard - 50,000 ppm of Absolute Standards or equivalent.

8.3 Surrogate Solution – o-Terphenyl, Tetracosane-d50, 5 α-Androstane 1000 ug/ml, Restek or equivalent.

8.4 Spike solution - Diesel stock standard - 20,000 ppm of Absolute Standards or equivalent.

8.5 C8-C44 Standard Solution 500μg/ml each of the Restek or equivalent.

8.6 Unopened stock must be stored according to manufacturer's documented holding time and storage temperature recommendations.

8.7 After opened, stock standards must be replaced after 6 months or sooner if manufacturer expiration date comes first or comparison with quality control check samples indicates degradation.

9.0 INTERFERENCES

9.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

9.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other stages of sample processing. Refer to "The Preparation of Glassware for Extraction of Organic Contaminants" SOP for practices utilized in the extraction department.

9.3 Contamination from "carry over" may occur when high and low level samples are sequentially analyzed. The sample syringe must be rinsed with reagent water, or a suitable solvent between samples. When an unusually concentrated sample encountered, a solvent-blank should be analyzed to check for cross contamination. Low level samples immediately following high level samples should be verified.

9.4 Most polar interferences (animal fats, glycerides, "leaf hydrocarbons", etc.) may be removed with the silica clean up.

9.5 Sample should be taken with care, to prevent any portion of the collected sample coming in contact with the sampler's gloves. Since this can result in phthalate contamination.

10.0 CALIBRATION

10.1 Initial calibration.

10.1.1 A minimum of five calibration standards are required although six are generally used. The concentrations are 100, 250, 500, 1000, 2000, 5000, 10,000, 50,000 μg/ml. The standards are prepared in Methylene chloride. Refer to the standards preparation logbook for procedure.

10.1.2 The initial calibration is performed with alkane standard C8-C44.

- to identify hydrocarbon range for client special requirement and

- for retention marker (see section 11 for detail).

10.1.3 The method reporting limit is established by the concentration of the lowest standard analyzed during initial calibration. The linear range covered by this calibration is equal to the highest concentration standard.

10.1.4 Aliquot proper amount of each calibration standard into a 2 ml crimp top vial.

10.1.5 Analyze the standard solutions using the conditions established in Section 12.0. Establish the calibration factor for each standard solution by dividing the total area of each standard by the total concentration as defined in Section 14.2.

10.1.6 For the initial calibration to be valid, the percent relative standard deviation (% RSD) (Section 14.3) must be less than 20 %. If the average calibration factor criteria cannot be achieved, corrective action must be taken.

10.1.6.1 If the problem is associated with a single standard, reanalyze the standard and recalculate the RSD.

10.1.6.2 Alternatively, narrow the calibration range by removing one of the calibration standards, but you still must have at least five standards.

10.1.6.2.1 The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

10.2 Initial Calibration Verification (ICV) – Second Source Calibration Check

10.2.1 A second source calibration check prepared at the concentration of 1000 µg/ml must be run immediately after the initial calibration.

10.2.2 The percent different (%D) (Section 14.4) for this standard must meet the criteria of 15% used for the calibration verification.

10.2.2.1 If the %D is greater than 15 %, reanalyze the second source check. If the criteria cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.2.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards by using one of the two standard sources that matches each other.

10.3 Continuing calibration checks

10.3.1 The initial calibration curve must be verified by a calibration check standards every 10 injections or 12 hours , whichever is more frequent. The concentration of the calibration check solution is alternated between concentrations of 500 µg/ml and 1000 µg/ml.

10.3.2 C8-C44 hydrocarbon standard is injected everyday to identify the retention window for integration of DRO range. If the retention time of the daily marker standard is outside the window, refer to section 10.3.6.

10.3.3 For the continuing calibration to be valid, the percent difference (%D) must be within 15% of the initial calibration factor. Calculate the percent difference (%D) using the following formula in Section 14.4.

10.3.4 Each sample analysis must be bracketed by periodic analyses of acceptable calibration verification standards. If %D criteria fails during a mid-sequence calibration check or at the end of the analysis sequence, a continuing calibration check is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed and the samples may need to be reanalyzed. In situations where the first check fails to meet the criteria, the instrument logbook should have clear documented notations as to what the problem was and what corrective action was implemented to enable the second check to pass.

10.3.5 When a calibration verification standard fails to meet the QC criteria at the end of the analysis sequence, all samples injected after the last standard that last met the QC criteria must be evaluated to prevent mis-quantitations, and re-injection of the sample extracts may be required.

10.3.5.1 If an analyte was not detected in the specific samples analyzed during the analytical shift, and then the extracts for those samples do not need to be reanalyzed when the calibration standard response is above the initial calibration response.

10.3.5.2 Whether the analyte was detected in the specific samples analyzed during the analytical shift, or the calibration standard response is below the initial calibration response, then the extracts for those samples need to be reanalyzed.

10.3.6 Each subsequent injection of a continuing calibration standard must be checked against the retention time windows established in Section 11.0. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

11.0 RETENTION TIME WINDOWS

11.1 The retention time range for DROs is defined during initial calibration. The range is established from the retention times of the C_{10} and C_{28} alkanes (the standard however contains C_8 –C_{44} hydrocarbons.) Use the following procedure to establish the retention time window from retention time studies performed using these two compounds. The retention time range is then calculated based on the lower limit of the RT window for the first eluting component and the upper limit of the RT window for the last eluting component.

11.2 Retention Time Determination

11.2.1 Perform initial retention time study using alkane markers. Analyze three calibration studies over a 72 hour period to maximize the retention time variability

11.2.2 Calculate the average retention time and standard deviation of the retention time for the C_{10} and C_{28} alkane marker compounds.

11.2.2.1 Establish the low end of the retention window for the DRO range using the lower extreme of the C_{10} alkane. Calculate this value at -3 times the standard deviation of the mean absolute retention time from the analysis conducted during the 72-hour period.

11.2.2.1.1 If the standard deviation is less than 0.01 minutes, employ a default minimum standard deviation of 0.01 minutes. If the default standard is used, the width of the window will be 0.03 minutes.

11.2.2.2 Establish the high end of the retention window for the DRO range using the higher extreme of the C_{28} alkane. Calculate this value at +3 times the standard deviation of the mean absolute retention time from the analysis conducted during the 72-hour period.

11.2.2.2.1 If the standard deviation is less than 0.01 minutes, employ a default minimum standard deviation of 0.01 minutes. If the default standard is used, the width of the window will be 0.03 minutes.

11.2.2.3 Document the retention time study and retain the retention time data as paper copy at the instrument.

11.2.3 Apply retention window data to the marker compound standards injection following initial calibration, using the lower extreme value for the low molecular weight compound and the higher extreme value for the higher molecular weight compound.

11.3 Check the window on calibration verification with the marker compound standard.

11.3.1 Update the retention time data in the quantitation method file using the new information. Use this window for the qualitative identification of diesel range organics in samples, standards, and quality control samples.

11.3.2 If the retention time of the daily marker standard is outside the window, recalibrate the instrument.

11.3.3 Retain documented records of all retention time information. Documentation may include paper file maintained next to each instrument or electronic data files that are archived for future use.

12.0 PROCEDURE

12.1 Instrument conditions. Recommended instrument conditions are listed in Table 1. Modifications are allowed as long as criteria of calibration are met and approved by team leader/manager.

12.2 Sample Preparation.

12.2.1 Aqueous samples are solvent extracted using liquid/liquid extraction procedures following method SW3510 – Separatory Funnel (Accutest EOP-001).

12.2.2 Soil/Sediment samples are solvent extracted using liquid/solid extraction procedure, SW3545-Pressurized Fluid Extraction(Accutest EOP040).

12.2.3 Refer to Accutest Organic Preparation SOPs referenced above for procedural details.

12.3 Initial Calibration. See Section 10.1.

12.4 Initial Calibration Verification (ICV). See Section 10.2.

12.5 Continuing calibration checks. See Section 10.3.

12.6 Instrument Blank.

12.6.1 An instrument blank is a volume of clean methylene chloride spiked with 5α-Androstane.

12.6.2 At the beginning of each 12-hour shift or immediately after the continuing calibration check, an instrument blank is injected to demonstrate that interferences from the analytical system are under control.

12.6.3 Acceptance Criteria

12.6.3.1 The DRO concentration in the instrument blank must be less than 100 μg/ml.

12.6.4 If the instrument blank does not meet the acceptance criteria above, then corrective action must be taken to locate and reduce the source of contamination. An acceptable instrument blank must be run before the analysis can proceed.

12.7 Sample analysis.

12.7.1 Inject 1 or 2 ul of the sample extract.

12.7.2 The DRO concentration (Section 14.5) is based on the total area of all peaks eluting between C_{10} and C_{28} minus the surrogate area and is calculated by external standard technique. If the concentration is greater than full scale of highest standard, then dilute and reanalyze the extract.

12.7.3 Preparing Dilutions.

12.7.3.1 Prepare sample dilutions quantitatively. Dilute the sample extract with methylene chloride using logical volume to volume ratios, i.e., 1:2, 1:5, 1:10, 1:50, etc. See Table 2 for dilution sequence. All dilutions must be made with a calibrated 1ml syringe.

12.8 Baseline correction for gas chromatography hydrocarbon methods is employed for GC methods that quantify total or fractional hydrocarbon ranges by integrating a retention time range that extends over several minutes. The potential for interfering peaks can occur from column bleed or common laboratory fragments, which can result in a positive bias in samples.

12.8.1 Minimize column bleed or chromatographic baseline rise by conditioning and replacing columns when necessary (i.e. when bleed becomes evident that may contribute to a positive bias in samples).

12.8.2 Integrate samples at a baseline that corresponds with the chromatographic profile of the associated instrument batch's instrument blanks.

12.8.3 If the instrument blanks display a chromatogram profile that cannot be isolated or may impact the area of associated samples, the blank is integrated and subtracted from samples.

12.8.3.1 Subtraction is performed by multiplying sample concentration the by the ratio of corrected area (sample area – blank area) divided by uncorrected sample area.

12.8.4 Corrected concentrations must be edited in the laboratory database (LIMS). Comparisons must be made between quantitation reports and LIMS printouts to eliminate transcription errors.

13.0 QUALITY ASSURANCE

13.1 QC Requirements Summary.

Initial Calibration Verification	Following initial calibration.
Calibration Verification Standards	Every 10 injections not to exceed 12 hours
Instrument Blank	At the beginning of each 12- hour shift or right after CCV
Method Blank	One per extraction batch
Matrix Spike	One per extraction batch*
Matrix Spike Duplicate	One per extraction batch*
Blank Spike	One per extraction batch*
Surrogate	Every sample and standard

*The maximum number of samples per analytical batch is twenty.

13.2 Initial Calibration verification (ICV).

13.2.1 Refer to Section 10.2.

13.3 Calibration Verification Standards.

13.3.1 Refer to Section 10.3.

13.4 Instrument Blank.

13.4.1 Refer to Section 12.6.

13.5 Method Blank

13.5.1 A method blank is a volume of a clean reference matrix (reagent water for water samples, or purified sodium sulfate for soil/sediment samples) that is carried through the entire analytical procedure. The volume or weight of the reference matrix must be approximately equal to the volume or weight of samples associated with the blank. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

13.5.2 A method blank must be extracted each time samples are extracted. The number of samples extracted with each method blank shall not exceed 20 field samples.

13.5.3 Acceptance Criteria

13.5.3.1 The concentration of each target compound in the method blank must be less than its MDL.

13.5.3.2 Surrogate recoveries must fall within the established acceptance criteria for the analysis.

13.5.4 Corrective Action

13.5.4.1 If a method blank does not meet the acceptance criteria, the system is out of control.

13.5.4.1.1 If contamination is a problem, then the source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. All samples associated with a contaminated method blank must be re-extracted and reanalyzed.

13.5.4.1.2 If the surrogate recoveries in the method blank do not meet the acceptance criteria, first reanalyze the method blank. If surrogate recoveries do not meet the acceptance criteria after reanalysis, the method blank and all samples associated with that method blank must be re-extracted and reanalyzed.

13.6 Blank Spike

13.6.1 A blank spike must be extracted with each set of 20 or less samples. The blank spike consists of an aliquot of a clean matrix (deionized water for aqueous samples or sodium sulfate for soil samples) similar to the sample and of the same weight or volume. It is spiked at the concentration of 1000 µg/ml or 100 mg/kg and is extracted and run through analytical procedures along with the other samples to monitor the efficiency of the extraction.

13.6.2 The blank spike recoveries and surrogates (Section 14.6) should be assessed using in house limits. These limits are determined annually, hard wired into the LIMS and used for QC decision purposes. If a blank spike is out of control, the following corrective action must be taken and all the associated samples may be re-extracted and reanalyzed. The exception is if the blank spike recovery is high and no hits reported in associated samples and QC batch. In that case, the sample results can be reported with footnote and no further action is required.

13.6.2.1 Check to be sure that there are no errors in the calculations, or spike solutions. If errors are found, recalculate the data accordingly.

13.6.2.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the sample batch.

13.6.2.3 If no problem is found, re-extract and reanalyze the sample batch.

13.7 Matrix Spikes /Matrix Spike Duplicates.

13.7.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike/matrix spike duplicate (MS/MSD) pair, a matrix spike to assess the impact of sample matrix on spike recovery, and a matrix spike duplicate to evaluate the precision associated with analysis of the matrix. The matrix spikes and matrix spike duplicates are spiked at a concentration in the mid-range of the calibration curve (1000 µg/ml or 100 mg/kg).

13.7.2 The acceptance range for matrix spike recoveries (Section 14.6) and relative percent difference (RPD) (Section 14.7) are statistically determined using in-house data. These limits (Appendix I) are determined annually, hard wired into the LIMS and used for QC decision purposes.

13.7.3 If matrix spike recovery does not meet acceptance criteria, the laboratory must assess the batch data to determine whether the spike results are attributable to matrix affect, or the result of other problems in the analytical process. If the blank spike is in control, and if there is no evidence that spiking was not properly performed, matrix interference is assumed and the data is reportable. No further corrective action is required. Otherwise, the method is out of control and the matrix spike sample(s) must be re-processed through the entire analytical sequence.

13.8 Surrogates.

13.8.1 All blanks, samples, QC samples, and calibration standards contain surrogate compounds to monitor the efficiency of the extraction and analytical procedures.

13.8.2 The recoveries (Section 14.6) of the surrogates must be evaluated versus the surrogate control limits developed by the laboratory.

13.8.3 If surrogate recovery is not within established control limits, corrective action must be performed.

13.8.3.1 Check the surrogate calculations for calculation or integration errors and perform corrections if detected. Reanalyze the extract if calculation errors are not detected.

13.8.3.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and reanalyze the extract.

13.8.3.3 If the surrogate recoveries for the reanalyzed extract are in control, report data from the reanalysis only.

13.8.3.4 If data from the reanalysis is also out of control, re-extract and reanalyze the sample.

13.8.3.5 If, upon reanalysis, the surrogate recoveries are acceptable, report the reanalysis data. If the holding time has expired prior to the reanalysis, report both the original and reanalysis results and note the holding time problem.

13.8.3.6 If the recovery is again not within limits, the problem is considered to be matrix interference. Submit both data sets with the original analysis being reported.

13.8.4 The retention time shift for surrogate must be evaluated after the analysis of each sample. The sample should be reanalyzed when the retention time of any surrogate compound is outside the retention window.

13.8.4.1 If the sample exhibits visible matrix interference, defined as excessive signal levels from target or non-target interfering peaks. In this case, reanalysis may not be required following team leader/manager approval.

14.0 CALCULATIONS

14.1 Sum the areas of all the peaks eluting between the hydrocarbon range of C_{10} to C_{28}. Do not include the area of the surrogate and internal standard, if applicable. Consult the supervisor for any integration questions.

14.2 Calibration Factor (CF).

$$CF = \frac{A_s}{C_s}$$

where:
A_s = Total Area within Retention Time Range minus the Surrogate area.
C_s = Concentration of the compound being measured (µg/ml).

14.3 Percent Relative Standard Deviation (% RSD).

$$\%RSD = \frac{SD}{CF_{av}} \times 100$$

where:
SD = Standard Deviation
CF_{av} = Average calibration factor from initial calibration.

14.4 Percent Difference (%D).

$$\% D = \frac{|CF_{av} - CF_c|}{CF_{av}} \times 100$$

where:
CF_c = Calibration factor from continuing calibration check standard.

14.5 Concentrations (Conc.):

14.5.1 Aqueous Samples:

$$\frac{As \times Vf \times D}{CF_{av} \times Vi} = \text{Sample Conc. mg/l}$$

where:
As = Area for sample hydrocarbon range of C_{10} to C_{28} (corrected for surrogate)
Vf = Final Volume of total extract (ml).
D = Secondary dilution factor.
Vi = Initial volume of water extracted (ml).

14.5.2 Soil Samples:

$$\frac{As \times Vf \times D}{CF_{av} \times Wt \times \%SOL \times Vi} = \text{Sample Conc. in mg/kg}$$

where:
As = Area for sample (corrected for surrogate)
Wt = sample wt in grams

14.6 Percent Recovery (% R).

$$\% R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

14.7 Relative Percent Difference (% RPD).

$$\% \text{ RPD} = \frac{|C_{ms} - C_{msd}|}{(1/2)(C_{ms} + C_{msd})} \times 100$$

Where:
C_{ms} = Matrix Spike Concentration.
C_{msd} = Matrix Spike Duplicate Concentration.

15.0 DOCUMENTATION

15.1 Analytical Logbooks are used to record the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

15.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in the Comments section.

15.2 The Standards Preparation Logbook must be completed for all standard preparations. All information must be completed, the page must be signed and dated by the appropriate person.

15.2.1 The Accutest lot number must be cross referenced on the standard vial.

15.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

15.4 Complete the sample data sheet, list the data files applicable to the sample batch, a photocopy of the instrument log in a folder labeled with the analysis, date and instrument number.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes

16.2.3 Chlorinated organic solvents

16.2.4 Non-chlorinated organic solvents

16.2.5 Hazardous solid wastes

16.2.6 Non-hazardous solid wastes

17.0 Data Review & Reporting

17.1 Initial and continuing calibration check. Verify that all calibration and continuing If samples had been analyzed under non-compliant calibration criteria, all sample extracts must be re-analyzed once the system is brought into control.

17.2 Quality Control Data Review. Review all QC data. If QC criteria were not achieved, perform corrective action before proceeding with analysis.

17.2.1 In some situation, corrective action may demand that the entire sample batch be re-extracted and reanalyzed before processing data.

17.3 Chromatogram Review. The chromatogram of each sample is evaluated for target compounds.

17.3.1 Check specific retention time windows for each target compound for the presence of the target compound in each chromatogram.

17.3.1.1 Projects may require the reporting of different hydrocarbon ranges. Review the login to assure that the correct hydrocarbon range is reported.

17.3.2 Manual integration of chromatographic peaks must be identified by the analysts by initialing and dating the changes made to the report.

17.4 Transfer to LIMS. Following the initial screen review, transfer the processed data to the LIMS.

17.4.1 Print the processed data and compare the printed values to the original values to verify transfer accuracy.

17.4.2 If transfer errors occurred, the errors must be corrected before the data is re-submitted.

17.5 Hardcopy Print & Data Package Assembly.

17.5.1 After successful transfer is verified, approve the data and print a hard copy.

17.5.2 Assemble the data package combining the LIMS output and instrumental data.

17.5.3 Pass the entire package forward to the supervisor for final review and release approval.

TABLE 1 Recommended Instrument Operating Conditions	
The conditions listed are a guideline, and should be optimized for the instrument and column in use.	
GC Conditions	
Instrument	HP 6890 or 7890
Column	30m x 0.25mm DB-5, 0.5µm film
Carrier	Helium @ 12 psig, 6 ml/min
Temp. Program	35°C for 5 min., 10/min. to 310°C (hold 15mins)
Detector	Flame Ionization
Make-up Gas	Helium @ 25 ml/min
Hydrogen	10 ml/min. Air: 300 ml/min
Injector Temp	300°C
Detector Temp	330°C

Table 2
Sample Dilution Table

All dilutions must be made using a 1ml calibrated syringe.

Dilution	*Intact Sample*	*Solvent*
1:2	500ul	500ul
1:5	200ul	800ul
1:10	100ul	900ul
1:20	50ul	950ul
1:25	40ul	960ul
1:50	20ul	980ul

Two Step dilution

Dilution	Step 1		Step 2	
	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*
1:100	100ul	900ul	100ul	900ul
1:200	100ul	900ul	50ul	950ul
1:250	100ul	900ul	40ul	960ul
1:500	100ul	900ul	20ul	980ul

Three Step Dilution

Dilution	Step 1		Step 2		Step 3	
	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*	*Sample Aliquot from Step 2*	*Solvent*
1:1000	100ul	900ul	100ul	900ul	100ul	900ul
1:2000	100ul	900ul	100ul	900ul	50ul	950ul
1:2500	100ul	900ul	100ul	900ul	40ul	960ul
1:5000	100ul	900ul	100ul	900ul	20ul	980ul

Four Step Dilution

Dilution	Step 1		Step 2		Step 3		Step 4	
	Intact Sample	*Solvent*	*Sample Aliquot from Step 1*	*Solvent*	*Sample Aliquot from Step 2*	*Solvent*	*Sample Aliquot from Step 3*	*Solvent*
1:10,000	100ul	900ul	100ul	900ul	100ul	900ul	100ul	900ul
1:20,000	100ul	900ul	100ul	900ul	100ul	900ul	50ul	950ul
1:25,000	100ul	900ul	100ul	900ul	100ul	900ul	40ul	960ul
1:50,000	100ul	900ul	100ul	900ul	100ul	900ul	20ul	980ul

ACCUTEST LABS
STANDARD OPERATING PROCEDURE

Lab Manager Nancy Cole

QA Manager Mary Jankowski

Effective Date: 4/29/13

TEST NAME: ALKALINITY, TOTAL (pH 4.5)

METHOD REFERENCE: SM2320 B-2011 (online edition of Standard Methods for the Examination of Water and Wastewater.) Soils by a modification of SM2320 B-2011

Revised Sections : ***8.8, 10.0, 10.1 (all), 10.2 (all) should to must***

1.0 SCOPE AND APPLICATION

1.1 Alkalinity is the measure of the acid-neutralizing capacity of a water sample, as the sum of all titratable bases. Since the alkalinity of surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it may be used as an indicator for the concentration of these constituents. The measured value will also include some borates, phosphates, silicates and other bases if they are present. The sample is not to be diluted, filtered, or altered in any way. This method is applicable for all water samples.

1.2 For samples of low alkalinity (<20 mg $CaCO_3$/l) an extrapolation technique is used. The amount of acid to lower the pH exactly 0.3 pH units is measured, after the initial endpoint has been attained. Because this corresponds to an exact doubling of the hydrogen ion concentration, an extrapolation may be made to the equivalence point.

1.3 Phenolpthalein alkalinity can be done following the same method using an endpoint of 8.3.

1.4 The product used in the LIMS system for this test is ALK.

1.5 The alkalinity of a neutral extract of a soil sample may also be analyzed following a modification of this method.

2.0 SUMMARY OF METHOD

2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method has been established at 5.0 mg/l.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's)

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory must initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits must also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs must be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 The samples must be stored in a refrigerator at 4^0 C.

6.2 Samples must be analyzed within 14 days of sample collection. Note: If Alkalinity is being done to calculate CO2, then it must be done immediately after collection or as soon as possible (with 24 hours) after receipt at the lab.

7.0 INTERFERENCES

7.1 Samples that contain oil, soaps or suspended solids may coat the electrode and cause a sluggish electrode response. Allow additional time between measurements to reach equilibrium at the electrode.

8.0 APPARATUS

8.1 pH meter with glass electrode capable of reading 0.05 pH unit.

8.2 Titration vessel, 100 ml or 200 ml beaker.

8.3 Magnetic stirrer; stirbars.

8.4 Pipettes, class A.

8.5 Volumetric flasks, class A.

8.6 Burets, 50 m and 10 ml micro.

8.7 20 liter carboy. 20 liter mark verified volumetrically with Class A glassware.

8.8 Wrist action shaker.

9.0 REAGENTS

9.1 Sodium Carbonate solution, approximately 0.05 N:Place 2.5 + or - 0.2 g (weigh to nearest 0.1 mg) of sodium carbonate (Na_2CO_3, dried at 250° C for 4 hours and cooled in a desiccator) into a 1 liter flask and dilute to the mark. Do not store for more than 1 week.

9.2 Standard Acid, 0.1 N. This solution must be standardized a minimum of once per quarter.

9.2.1 Sulfuric acid: Add 56 ml of concentrated H_2SO_4 to approximate 10 liters of DI water in a 20 liter carboy. Dilute to 20 liters with DI water and mix well. (This can also be done on a smaller volume, using 2.8 ml of concentrated sulfuric to a final volume of 1 liter in a volumetric flask.)

9.2.2 Hydrochloric Acid (not normally used, but an acceptable alternative): Add 8.3 ml of concentrated HCl to 500 ml DI water in a 1 liter volumetric Flask. Dilute to 1 liter with water.

9.3 Standard Acid 0.02 N: Dilute 200.0 ml of 0.1 N Standard Acid (use 9.2.1 or 9.2.2) to 1 liter with distilled water. This solution must be standardized a minimum of once per quarter.

9.4 Sodium Phosphate, dibasic: 0.10 M Weigh 26.81 g of sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$). Dissolve in approximately 600 ml of DI water in a 1000 ml volumetric flask. Dilute to 1 liter. Alkalinity value is 5000 mg/l as $CaCO_3$.

9.5 Sodium Phosphate dibasic, 0.005 m: Dilute 5 ml of 0.10 m sodium phosphate to 100 ml. Alkalinity value is 250 mg/l as $CaCO_3$.

10.0 SOIL SAMPLE PREPARATION PROCEDURE

10.1 For soil samples, weigh out 20 g of sample and, using a class A graduated cylinder, add 200 ml of DI water. Shake using a wrist action shaker for ten minutes.

10.1.1 For the method blank, measure out 200 ml of deionized water and shake using the wrist action shaker for ten minutes.

10.1.2 For the spike blank, use 200 ml of the sodium phosphate dibasic, 0.005 m solution described in section 9.5. Shake on a wrist action shaker for ten minutes.

10.2 Filter the resulting slurry through a Whatman GFB or GFF filter (or equivalent). Note: All QC must be shaken and filtered in the same method as the samples. Analyze for Alkalinity following section 11.0

11.0 PROCEDURE

11.1 If the acid solution has not been standardized within the last 3 months, then it must be restandardized before starting the analysis. The procedure for standardizing the 0.10 N and 0.02 N acid solutions is shown below.

11.1.1 Calibrate the pH meter according to manufacturer's instructions, and document the calibration in the pH meter logbook and on the alkalinity worksheet. Read back the 4, 7, and 10 buffers. If the results are not within 0.05 pH units, then the meter must be recalibrated before proceeding.

11.1.2 Rinse the 50 ml buret with approximately 20 ml of standard acid, then fill it and adjust volume to 0.0.

11.1.3 If standardizing the 0.10 N acid solution, add 40.0 ml of 0.05N Sodium Carbonate Solution to about 60 ml of distilled water in a 250 ml baker. If standardizing the 0.02 N acid solution, add 15.0 ml of 0.05N sodium carbonate solution to about 60 ml of distilled water in a 250 ml baker.

11.1.4 Add a stir bar and place on a magnetic stirrer. Mix gently.

11.1.5 Place pH probe in the sodium carbonate solution and titrate to a pH of approximately 5. Record the pH after every 0.5 ml acid addition. Remove electrode and rinse in beaker of sodium carbonate.

11.1.6 Cover the beaker with a watch glass and boil the solution for 3- 5 minutes. Allow to cool.

11.1.7 Continue the titration to the pH inflection point and record the pH after every 0.2 ml addition. Continue the titration to pH 3.0.

11.1.8 Plot the pH of the sodium carbonate vs. ml of acid added.

11.1.9 Calculate the normality of the acid as shown below. If the normality varies by more than 10% from the expected normality, than new acid must be made and restandardized.

Normality N =

$$\frac{A \times B}{53.00 \times C}$$

Where:
A = g Na_2CO_3 weighed
B = ml Na_2CO_3 solution
C = ml Acid used at inflection point.

11.2 Procedure for analysis of samples with alkalinity values above 20 mg/l.

11.2.1 Place 100 ml of the sample in the titration vessel (beaker or flask), with minimal agitation. Place a stir bar in the titration vessel.

11.2.2 While stirring gently but thoroughly, measure the pH of the sample. Record the pH on the analysis log.

11.2.3 Slowly add 0.02 N standard acid allowing the pH meter to achieve equilibrium between additions.

11.2.4 Titrate the sample to a final pH of 4.5. Record the volume of acid used for the titration on the analysis log.

11.3 Procedure for the analysis of samples with alkalinity values below 20 mg/l (< 2.0 ml of 0.02 N titrant)

11.3.1 Titrate the sample as described in 10.2.1 through 10.2.4, using a 10 ml microburette and 0.02 N titrant.

11.3.2 Stop the titration in the pH range of 4.3 to 4.7 and record the volume used.

11.3.3 Very carefully add titrant to lower the pH 0.3 pH units and again record the volume.

11.4 For samples with a concentration above 20 mg/l, use the following calculation to calculate the alkalinity.

$$\text{Alkalinity , mg/l } CaCO_3 = \frac{A \times N \times 50000}{\text{ml sample}}$$

Where: A = ml of standard acid
N = Normality of standard acid

11.5 For Samples with a concentration below 20 mg/l, use the following calculation:

$$\text{Alkalinity, mg.l } CaCO_3 = \frac{(2A - C) \times N \times 50000}{\text{ml sample}}$$

Where: A = ml titrant to first pH
C = total ml titrant to reach pH 0.3 units lower
N = Normality of Acid.

11.6 After every 10 analyses, check the pH meter with the 4.0 pH buffer. The buffer must be within 0.20 pH units of 4.00.

11.6.1 If the check is outside of the 0.20 pH unit criteria, check the probe for problems. If the problems are unrelated to the sample matrix, then resolve the problems and reanalyze the samples and the check standards.

11.6.2 If the 0.20 pH unit criteria cannot be met due to difficulties with the probe caused by the sample matrix, see the area manager or supervisor. Sample results may be reported with a footnote noting the recovery obtained on the check standard.

12.0 QUALITY CONTROL

12.1 The 4, 7, and 10 buffer solutions must be checked prior to the analysis of the samples. The results of these buffer checks must be within 0.05 pH units of the true values. If they are not, then recalibrate the pH meter before proceeding.

12.2 An external check must be analyzed at least once per quarter or whenever the primary standard lot changes. The results of the external check must be within manufacturer's limits, or, if no limits are supplied, within 10%.

12.3 A buffer check standard must be analyzed after approximately every 10 samples. This check must be within 0.2 pH units of the true value. Refer to section 10.6 for the appropriate action to take if the check is outside of these limits.

12.4 When analyzing samples, a duplicate sample must be analyzed with each group of 20 samples. This quality control point must be evaluated using Accutest's in house quality control limits. Note: if the in house limits are not available, then the default limit of 20 rpd must be used.

12.5 A method blank and a spike blank must be analyzed with each batch of 20 samples or daily, whichever is more frequent. The method blank results must be < RDL and the spike blank must have a recovery in the range of 90 to110 % recovery. If this criterion is not met, then the samples must be reanalyzed.

13.0 DOCUMENTATION REQUIREMENTS

13.1 The analyst must document all relevant information, including, but not limited to, all sample volumes, all initial and final pH values, and any relevant comments for any section of the analysis. Make sure to record any comments regarding unusual sample appearance or any other problems or observations. All reagent and standard information, including the manufacture, lot, and expiration date must be recorded in a reagent log. In addition, the pH meter that was used and the buffer solutions used must be documented. All work must be dated and signed by the analyst. Any changes must be crossed out with a single line and must be initialed and dated and a reason for the change provided.

14.0 DATA REVIEW AND REPORTING

14.1 All samples must be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for making sure that the raw data is fully documented and it is updated and entered in the LIMS system.

14.2 After the analyst review is completed, the supervisor or a designated reviewer must review the data for technical compliance to the SOP. After the reviews are completed, the data is electronically filed in the report generation department.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT.

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

15.0 ADDITIONAL REFERERENCES

15.1 Refer to pH meter manuals for operation of individual pH meters and for care of pH probes.

Accutest Laboratories
Standard Operating Procedure

Lab Manager_____

QA Manager_____

Effective Date: _____

TEST NAME: METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP).

METHOD REF: SW846 6010B

Revised Sections: ***modified 10.12, 10.15, 12.4.1, 12.13. Modified Table 1, Table 4.***

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of metals in water, wipes, sludges, sediments, and soils. Sample matrices are pretreated following SW846 methods for digestion of soil, sediment, sludge, wipe or water samples. Refer to specific digestion SOP's for more information on digestion techniques.

1.2 A variety of metals can be analyzed by ICAP. These include Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Si, Ag, Na, Sr, Tl, Sn, Ti, Pd, V, and Zn. Lower detection limits can be obtained for metals such as As, Pb, Sb, Tl, and Se using the Trace ICP

2.0 SUMMARY

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multi-elemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background intensity as 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. The possibility of additional interferences named in Section 7.0 should also be recognized and appropriate corrections made. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The normal reporting limits for this method have been established at the concentrations listed in Table 1. Reporting limits may vary depending on client needs and lab protocols, but the reporting limits must always be verified with a low check which meets the criteria outlined in this SOP. In addition the reporting limit must always be greater than the MDL. Refer to the scheduling sheets and check with the metals supervisor for further information.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent or every 2 hours during an analysis run, whichever is more frequent, and at the end of the analysis sequence. For this method, the mid-level calibration check standard criteria is ± 10 percent of the true value and the relative standard deviation for the replicates that are greater than 5 times the reporting limit is less than 5 percent. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the reporting limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses. It is recommended that this check be analyzed at the start of each run. For this method, the external check standard criteria is ± 10 percent of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. For a running batch, a new lab control sample or spike blank is required for each different digestion day. Assess laboratory performance against the control limits of 80 to 120 percent. In house limits should also be generated once sufficient data (usually a minimum of 20 to 30 analyses) is available to support the default limits. For solid lab controls, the elements should be within the range given by the lab control supplier. If the lab control or spike blank is outside of the control limits for a parameter, all samples must be redigested and reanalyzed for that parameter. The exception is if the lab control or spike blank recovery is high

and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX SPIKE DUPLICATE: A matrix spike duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the matrix spike duplicate and the matrix spike should be assessed. A duplicate may be used in place of the matrix spike duplicate on client request. The matrix spike duplicate RPD is calculated as shown below. The control limit for the duplicate is 20% rpd. If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

$$\frac{(|\text{Matrix Spike Result} - \text{Matrix SpikeDuplicate Result}|) \times 100}{(\text{Matrix Spike Result} + \text{Matrix Spike Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the default limits of 75 to 125 percent. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS).. The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10

times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analysis.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All water samples should be preserved with nitric acid to a pH of 2 or less. All solid samples should be stored in a refrigerator at 4 degrees C.

6.2 All samples should be analyzed within 6 months of the date of collection.

7.0 INTERFERENCES

7.1 Several types of interferences can cause inaccuracies in trace metals determinations by ICP. These interferences are discussed below.

7.2 Spectral interferences are caused by overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and background contribution from stray light from the line emission of high concentration elements. Corrections for these interferences can be made by using interfering

element corrections, by choosing an alternate analytical line, and/or by applying background correction points.

7.3 Physical interferences can be caused by changes in sample viscosity or surface tension, by high acid content in a sample, or by high dissolved solids in a sample. These interferences can be reduced by using an internal standard, by making sample dilutions or by analyzing a sample using the method of standard additions.

7.4 Chemical interferences are not pronounced with ICAP due to the high temperature of the plasma, however if they are present, they can be reduced by optimizing the analytical conditions (i.e. power level, torch height, etc.).

8.0 EQUIPMENT AND SUPPLIES

8.1 Currently there are three ICPs available for use in the lab, however this SOP is specific to the Thermo Trace ICP. This unit is a simultaneous unit. It has been optimized to obtain low detection limits for elements such as Sb, As, Se, Pb, and Tl. This optimization was done using a horizontal torch, a purged optics system, optimized photomultiplier tubes, and Crawford-Kunselman Noise Reduction techniques. The lines programmed into the Trace 3 system are shown in Table 2.

8.2 Instrument autosamplers. For random access during sample analysis.

8.3 Class A volumetric glassware and pipets.

8.3.1 All glassware must be washed with soap and tap water and then soaked in a 10% nitric acid bath for several hours. It must then be rinsed at least 3 times with deionized water.

8.4 Glass autosampler tubes

8.4.1 Autosampler tubes must be washed with soap and tap water and then soaked in a 50% nitric acid bath for several hours. They must then be rinsed at least 3 times with deionized water.

8.5 Autopipeters with tips. These must be calibrated and checked as outlined in the autopipeter SOP, EQA004.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required. The expiration date for standards and reagents is the date supplied by the manufacturer or if no expiration date is given, a default of 6 months is used. For acid solutions (nitric, sulfuric, hydrochloric) the expiration date is 2 years from the date of preparation of the solution.

9.2 Hydrochloric acid, trace metals grade.

9.3 Nitric Acid, Baker instra-analyzed or equivalent.

9.4 Standard stock solutions available from Absolute, Inorganic Ventures, MV Laboratories, Ultra Scientific or equivalent. Note: All standards must be ICP quality standards.

9.5 Calibration Standards. These can be made up by diluting the stock solutions to the appropriate concentrations. Since calibration standards are made fresh daily, they can be stored in volumetric glassware. (Any stocks or other check samples should be placed in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for long term storage.)

9.5.1 Standards should be approximately matrix matched to the samples. For most samples, a 3 percent nitric acid and 5 percent hydrochloric acid will approximate the acid matrix of the sample and limit nebulization problems. If it is known that the samples contain a significantly different acid matrix, then the matrix of the standards should be modified or the samples should be diluted so that they are in a similar matrix to the curve.

9.5.2 Standards should be prepared so that there is minimal spectral interference between analytes.

9.5.3 Refer to the standards book for the make-up and concentrations of standards and stock solutions being used to calibrate the ICP. Levels for the standards are shown in Table 3. The calibration curve should consist of a minimum of a blank and a standard.

9.6 Calibration/Rinse Blank. The calibration blank is prepared by diluting a mixture of 30 ml of concentrated nitric acid and 50 ml of concentrated hydrochloric acid to a final volume of 1 liter with deionized water.

9.7 Analytical Quality Control Solutions. All of the solutions below are prepared by adding either mixed or single element metals solutions to a solution containing 3 percent nitric acid and 5 percent hydrochloric acid and diluting to a fixed final volume with this acid mixture. All of these solutions should be placed in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for long term storage.

9.7.1 Initial Calibration Verification solution. This standard solution must be made from a different source than the calibration curve. The values for each element should be within the range of the calibration curve. This solution is used to verify the accuracy of the initial calibration. See Table 4 for suggested ICV concentrations.

9.7.2 Continuing Calibration Verification solution. The metals concentrations for this standard should be at approximately the mid-point of the calibration curve for each element. This standard should be prepared from the same source that is used for the calibration curve. See Table 4 for suggested CCV concentrations.

9.7.3 Interference Element Check Solutions. These solutions should be used on a periodic basis to check the interfering element corrections on the instruments. Note: If interferences from different elements than those listed below are a problem, the interfering element solutions may be modified. Two acceptable solutions are outlined below.

9.7.3.1 ICSA Solution. The ICSA solution contains only the interfering elements. The recommended concentrations are shown below. If the linear ranges on a given

instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements.

Al	500 mg/L
Ca	400 mg/L
Fe	200 mg/L
Mg	500 mg/L

9.7.3.2 ICSAB Solution. The ICSAB solution contains both the interferents and the analytes of interest. The recommended concentrations are shown below. . If the linear ranges on a given instrument are lower than these levels, the concentrations may be set near the top of the linear range for those elements

Ag	1.0 mg/L	Zn	1.0 mg/L
Ba	0.50 mg/L	As	1.0 mg/L
Be	0.50 mg/L	Se	1.0 mg/L
Cd	1.0 mg/L	Sb	1.0 mg/L
Co	0.50 mg/L	Tl	1.0 mg/L
Cr	0.50 mg/L	Mo	0.5 mg/L
Cu	0.50 mg/L	Pd	0.5 mg/L
Mn	0.50 mg/L	Al	500 mg/L
Ni	1.0 mg/L	Ca	400 mg/L
Pb	1.0 mg/L	Fe	200 mg/L
V	0.50 mg/L	Mg	500 mg/L

9.7.4 CRI Standards. The CRI standards contain the elements of interest at the lowest level that elements are to be reported. Note: This QC check is required for NELAC.

9.8 Matrix Spike and Spike Blank Solution (For soil samples). The final concentrations suggested for the matrix spike and spike blank solutions are shown in Table 5. The spiking solution is prepared by adding either mixed or single element metals solutions to a solution containing 2 percent nitric acid and diluting to a fixed final volume with this acid mixture. Two mls of this stock solution should be added to the spike blank and the matrix spike before they are digested and brought to a final volume of 100 ml.

9.9 Matrix Spike and Lab Control Solution (For aqueous samples and TCLP leachates).

9.9.1 The final concentrations suggested for the matrix spike are shown in Table 5. Two spiking solutions, which are used for aqueous samples and TCLP leachates respectively, are prepared by adding either mixed or single element metals solution to solutions containing 2 percent nitric acid and diluting to a fixed final volume with this acid mixture. 0.5 ml of the resulting stock solution is added to the matrix spike sample before they are digested.

9.9.2 A lab control sample should be digested and analyzed for every batch of 20 samples or less. The LCS is prepared by adding either mixed or single element metals solutions to DI water and bringing up to a fixed final volume. For TCLP samples, the lab control should be made using blank leachate solution rather than DI water. 50 ml of this solution is digested and brought to a final volume of 50 ml. In situations where any odd

elements, such as B, Si, Sr, Sn, and Pd, is of interest for a specific project, besides a lab control, a spike blank is also digested.

9.10 Liquid Argon or Argon Gas. Argon is provided by Air Products in the large outdoor tank. No lab monitoring of the tank is normally necessary

9.11 Internal Standard Solution (with matrix modifier).). To a 1 liter flask containing approximately 800 ml of DI water, add 10.0 ml of 10,000 mg/l Lithium solution and 0.500 ml of 10000 mg/l yttrium. Add 30 ml concentrated nitric acid and 50 ml concentrated hydrochloric acid and bring to a final volume of 1000 ml and mix well. This solution is added to all samples and standards as the instrument is running using a split line on the peristallic pump

10.0 PROCEDURE

10.1 General procedure on how to operate the TJA Trace is described below. Refer to the TJA Trace operation manual for further details. This SOP is specific to the ICP Manager 61 software, which can be accessed in a Windows environment.

10.2 Before bringing up the instrument, make sure that the lines, the torch, the nebulizer, and the spray chamber are clean, the dehumidifier is filled with DI water up to the level between Minimum and Maximum, and that there are no leaks in the torch area.

10.3 Turn on the recirculating cooler. Verify that the liquid argon is turned on.

10.4 Engage the peristaltic pump.

10.5 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover.) If internal standard is being used, make sure that sufficient internal standard solution is prepared.

10.6 Enter the ICP Manager 61 software and go to “Instrument”. From drop-down menu select Plasma Control Panel. Select “Startup”, then ‘Ignite”. Warm up the instrument at least one hour after it is lit. Please make sure the pump speed is at 130.

10.6.1 NOTE: While the instrument is warming up, the standards should be prepared and the samples that are to be analyzed should be collected together along with the required quality control.

10.7 After the instrument has warmed up, the nebulizer should be optimized. This routine is not required on a daily basis, but only when first setting up a new instrument, a new nebulizer or following a change in operating conditions. The procedures for the TJA Trace are given below.

10.7.1 The nebulizer position and pressure should be adjusted to achieve the highest signal to background ratio. To do this, go to Instrument, from drop down menu find Configuration. Select the method (e.g. EPA3) under “identifier”. Adjust the nebulizer pressure to the point between 25 and 35 PSI (normally approximately 28 psi) where the intensity is highest in relation to the lowest rsd. Then perform a profile (refer to Section 10.8) to obtain the highest ratio of signal intensity to background.

10.7.2 The torch placement optimization should also be checked whenever the torch is removed and replaced or whenever there is a decrease in sensitivity. This can be done using the following procedure. Aspirate a blank into the instrument and measure the intensity. Open the window and adjust the torch position using the manual thumb screws in the compartment to the left of the nebulizer compartment. The torch should be positioned to obtain the lowest intensity reading for the blank.

10.8 Next profile the instrument by aspirating a known concentration solution of an element. The element used for the profiling the instrument should be picked to minimize the element shifts for all of the elements in the method. Currently an arsenic solution of 5 ppm is used for the Trace profiling. Normally, the automatic profile program will properly profile the instrument. However, the manual profile program can be used if the instrument profile has drifted significantly. The profile can be done as an option in INSTRUMENT. From drop-down menu select AUTOMATED PROFILE. Select AS for Reporting Name. Make sure the current Vernier Setting is in the Vernier Setting box. You can either use auto sampler or manual injection to do the profile. If choose to use auto sampler, make sure the Tray name, Tray Position are selected correctly, and also select Use Autosampler Positioning. Click Next, then click Profile. If the New Position and Vernier Setting are satisfactory, save the result and adjust the vernier setting on the instrument.

10.8.1 On a daily basis, monitor the counts and the signal to noise ratio of the profile solution. This is instrument and nebulizer dependent, but a significant shift (greater than 10%) in these numbers for a given instrument and nebulizer indicates a possible change in instrument conditions that may affect analytical performance. Investigate shifts and verify that the instrument is meeting performance requirements before continuing with the run.

10.9 Before starting a daily run, always create a new sample list for the run. Go to Samples and select SAMPLE LIST EDITOR. From the drop-down menu select **EPA3** for Method, Reporting List and Routine. Name the Result File using the format I, instrument letter identifier (r for Trace1, p for Trace2, and t for Trace3), month, year, type of run (w for water, s for soil, m for mixed) and number of run. For example, the first mixed trace run from 3/08 would be named ir0308m1. From the drop-down menu select 300posG for Tray. In PDF Output, always check off **Enable** and use the same name for the PDF file as for the Result File for the day.

10.10 Calibrate the instrument as outlined below. Calibrate the instrument as outlined below using the standards shown in Table 3. This calibration procedure is done a minimum of once every 24 hours. The calibration standards may be included in the autosampler program or they may be run separately. If more than two standards are used, a correlation coefficient of 0.995 or better must be obtained using a first order curve fit. Second and third order curve fits are not acceptable.

10.10.1 Click on RUN A STANDARD. A screen will appear for you to choose the standard type, name and position. Select Calibration Standard for all the calibration standards and select STD as tube position. Insert all the calibration standards into the Sample list. At the end of all the calibration standards, perform Regression. A screen with all the elements will appear at this point. Make sure to check off Regress All Lines. Then click Check the Sequence for Errors to check any errors. If there are no errors, then click Queue the sample list and then click the green

button to start the sequence. For any elements whose correlation coefficients are less than 0.998, a window will appear to indicate the failure of the regression.

10.10.2 Go to Development and select Calibration Curve-fitting. Select “Baseline Calibration” on top left box. Select Autosave and highlight the element in Analyte box. Use arrow down key to go through the adjustment for all the elements to update the calibration.

10.10.3 If certain elements need to be recalibrated, insert the calibration standards you wish to recalibrate and apply Regression at the end of the additional standards. Once again, after the additional calibration standards are analyzed, perform a Regression. Make sure to only choose the elements you wish to calibrate, not all the elements.

10.11 After calibration is completed, go back to Sample List Editor. Open the file and start to add the QC points and samples for the run. Use Run a Standard to insert QC samples like CCV, CCB, CRI, ICSA, ICSAB, ICV, ICB, etc. Select Flexible QC for all of these types of QC samples in the list. Use Run an Unknown to insert all the real samples into the list. Run an Unknown should also be used to insert method blanks, spike blanks, matrix spikes, etc. Select TUBE for the tube position. At Sample ID 1, type in the sample ID such as MP12345-MB1, etc. At Sample ID2 type in the list pointer.

10.11.1 Check with the metals supervisors for additional information on the use of list pointers. In general, listpointer 2 refers to the SW846 6010 method and listpointer 1 refers to EPA 200.7 method.

10.12 Run the CRI solution after the calibration is completed and before any samples are analyzed.

10.12.1 For all samples, the CRI check solution must be at the reporting limit for each element. If special client reporting limits are requested, then low checks corresponding to those reporting limits must also be analyzed.

10.12.2 In house limits of 50 to 150% are applied to the CRI standard, but tighter criteria may be needed in some client or project specific situations.

10.12.3 For work following the DOD program code, an acceptance criteria of 80 to 120 percent must be applied to all elements whose RL is greater than 3 times the MDL unless a project specific waiver is obtained.

10.13 After the instrument is properly calibrated, begin by analyzing the ICV and ICB check standards. For the ICV, all elements to be reported must be within 10 percent of the true values. After the ICV and ICB and before any actual samples are analyzed, the CCV and CCB should be analyzed. For the CCV, all elements to be reported must be within 10 percent of the true values. For both ICV and CCV, all replicates exceed 5 times the reporting limit should have a relative standard deviation of less than 5 percent. Both ICB and CCB results should be less than three times the IDL or less than 1/10 of the concentration of the action level of interest. (ICB and CCB values should be less than the reporting limits for the elements).

10.13.1 For work following the DOD program code, the initial and continuing calibration blanks must be less than 2 times the MDL. Refer to section 12.2 for a definition of the MDL for this program.

10.14 Before analyzing any real samples, an interference check solution must be checked. For all spiked elements, the analyzed results must be within 20 percent of the true results. For unspiked elements, the interfering element solutions should contain less than the absolute value of two times the reporting limit for each element.

10.14.1 If the interfering element solution is not within specifications and that element must be reported, then new interfering element correction (IEC) factors will need to be generated following the procedure outlined in Section 11 below. If new IEC's are generated, then the run must be restarted from the ICSA, ICSAB quality control samples and new CCV checks must be run before any samples can be reported.

10.15 After the initial analytical quality control has been analyzed, the samples and the preparation batch quality control should be analyzed. Each sample analysis should be a minimum of 2 readings using at least a 5 second integration time. It is recommended that 3 readings be used for each sample analysis. For samples containing levels of elements greater than approximately 5 times the reporting limits, the relative standard deviations for the replicates should be less than 5%. If not, reanalyze the sample. If, upon reanalysis, the RSDs are acceptable, then report the data from the reanalysis. If RSD's are not acceptable on reanalysis, then the results for that element should be evaluated by the data reviewer and footnoted if necessary. In some cases, an additional dilution analysis may be needed. Check with the area supervisor or manager for additional information.

10.15.1 Use Run an Unknown to insert all the real samples including method blanks, spike blanks, matrix spikes, etc. Select TUBE for the tube position. At Sample ID 1 type in the sample ID such as MP12345-MB1, etc. At Sample ID2 type in the list pointer.

10.15.2 Every time you need to resume the analysis of an interrupted sequence, queue the sample list first, before start to run, make sure the most recently queued list is highlighted by Yellow color. You can also select a start point (otherwise it will start from the beginning of the sequence). Right click the mouse and select Start Point, then highlight the sample you wish to start.

10.16 Between each sample, flush the nebulizer and solution uptake system with a blank rinse solution for a minimum of 60 seconds or for the required period of time to ensure that analyte memory effects are not occurring. A time of 120 seconds is recommended for most analyses.

10.16.2 A rinse time of 96 seconds combined with the step-ahead function will give an approximate total rinse time of 120 second.

10.17 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth samples or every 2 hours during an analysis run, whichever is more frequent, and at the end of the sample run.

10.17.1 If the CCV solution is not within 10 percent of the true value, no samples can be reported in the area bracketed by the failing CCV for the failing element. Additionally, for the elements with a CCV greater than 5 times the reporting limit, the relative standard deviation for the replicates should be less than 5 percent.

10.17.2 The CCB results should be less than three times the IDL or less than 1/10 of the concentration of the action level of interest and less than the reporting limit. If the CCB does not meet this criterion and is less than the reporting limit, it can be reanalyzed two more times. The average of the three readings must be within 3 standard deviations of the background mean. If these criteria are not met, then no samples can be reported in the area bracketed by the failing CCB for the failing element. The exception is that samples that are less than the reporting limit may be reported if the CCB is biased high, but is still less than the reporting limit.

10.17.2.1 For work following the DOD program code, the initial and continuing calibration blanks must be less than 2 times the MDL. Refer to section 12.2 for a definition of the MDL for this program.

10.17.3 If the initial CCB is above the reporting limit, then all samples should be submitted for reanalysis. Do not rerun the CCB if the initial reading is above the reporting limit.

10.17.4 If reanalysis of the CCB is required, reanalyze a new pair of CCV, CCB before proceeding with the analysis of any additional samples.

10.18 For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, a serial dilution should be prepared. For the serial dilution, a 1:5 dilution should be made on the sample. The results of the 1:5 dilution should agree within 10 percent of the true value as long as the sample is greater than 50 times of the instrument detection limit for that element.

10.19 Post-digest spikes may also be used to determine potential interferences. Check with the metals supervisor for further information on when a post-digest spike should be performed.

10.20 For any readings that exceed the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. A verification may be necessary by rinsing the lines with an acid solution and then rereading the sample. A limit check table may be built into the autosampler file so that samples exceeding the linear range are flagged on the raw data.

10.21 For the interelement spectral interference corrections to remain valid during sample analysis, the interferent concentration must not exceed its linear range. If the interferent exceeds its linear range or its correction factor is big enough to affect the element of interest even at a lower concentration, sample dilution with reagent blank and reanalysis is required. In these circumstance analyte detection limits are raised. Check with metals supervisor for more information.

10.21.1 Anytime that the interference is large relative to the sample, dilution may be required. Check with the metals supervisor for more information.

10.22 For any readings where the internal standard is outside of the range of 60 to 125% of the internal standard level in the calibration blank, then the sample should be diluted until the internal standard is within that range.

10.23 This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required to meet other method and/or client requirements. Run

the ICSA and ICSAB solutions every 8 hours unless otherwise instructed by the metals lab supervisor or manager.

10.24 All the data are automatically saved during the analysis to **Results** file. Whenever the analyst needs to transfer the data into network during the run or at the end of the run, go to Desk Top, click Shortcut to Results and find the file to be transferred. Please note; do not transfer any file to the network when the instrument is analyzing a sample. It may cause a share violation resulting in the loss of data.

10.24.1 If any portion of a run needs to be reprinted due to printer problems or for any other reason, the analyst can go to Desk Top and click Shortcut of Reprint to print any data.

10.25 The data must be reviewed in the LIMS as outlined in the inorganic data review SOP, EQA034. Calculations for water samples are done automatically in the LIMS using the equation shown below.

original sample concentration of metal (μg/l) =

$$\frac{\text{(conc. in the digestate (}\mu\text{g/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

10.26 At the end of the analysis day the ICP must be brought down using the following sequence.

-Rinse the tip in a solution of 3 percent nitric acid and 5 percent hydrochloric acid for 10 minutes and in DI water for 20 minutes. (Note: a stronger acid solution may be needed depending on the matrix of the samples that were analyzed.)
-Turn off the plasma using the Plasma Control Option under the INSTRUMENT-PLASMA CONTROL PANEL.
-Release the tension on the pump tubing.
-Turn off the cool flow and the printer.
-Turn off the monitor.

11.0 PROCEDURE FOR GENERATION OF INTERFERING ELEMENT CORRECTION FACTORS

11.1 All IEC's must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly. It is recommended that elements with frequent high concentrations or with large IEC's should be checked more frequently.

11.2 Use Run a Standard to insert all the interference calibration standards, IEC Blank, Fe500, Al500, Ca500, Mg500, etc. Select Interference Calibration Standard as the standard type.

11.1.1 IEC correction factors are generated for all elements in a program using a standard at or near the linear range for that element. Al,Ca, Fe, and Mg correction factors are generated using 500 ppm single element solutions.

11.2 After all the standards are analyzed, go to Development-Calibration Curve-fitting. This time choose Interference Calibration in the top left box. Select Autosave and go through all the analytes and all the interfering elements to update the interference corrections.

11.3 When the analyst needs to perform a manual interference correction, go to Development-Method Explore. Go to EPA3 and then Interference Calibration, in the table find the interfering element and interfered element and make the change for C1.

11.3.1 Calculate the correction factor using the equation shown below. This correction factor must be added to the correction factor already in place in the method for a given element.

$$\text{IEC} = \frac{\text{Concentration Result of the element with the interference}}{\text{Concentration result of the interfering element}}$$

11.4 Double check that the correction factor is correct either by rerunning a single element or IEC solution.

11.5 Interfering element correction factors are printed out on a daily basis and a copy is attached to the raw data so that the IEC's used for a given run are traceable.

12.0 QC REQUIREMENTS

12.1 This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements for method SW846 6010B.

12.2 Method Detection Limits (MDLs). MDLs should be established for all analytes, using a solution spiked at approximately 3 to 5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.143, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

12.2.1 For work done following the DOD program code, if instrument performance indicates difficulties in achieving verification in the range of 50 to 150 percent at levels near the MDL, then quarterly MDL verification studies will be required. The verification level will then be used as the DOD MDL asessment level.

12.3 Instrument Detection Limits (IDLs). Instrument Detection Limits (IDLs). Although no frequency is given, it is required that IDL's be completed a minimum of once per year for all analytes or whenever instrument conditions have significantly changed. The Instrument Detection Limits (in ug/L) are determined by multiplying three times the standard deviation of 10 reading of a calibration blank. Each measurement shall be performed as though it were a separate analytical sample (i.e., each measurement shall be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs shall be determined and reported for each wavelength used in the analysis of the samples.

12.4 Linear Calibration ranges. The upper limit of the linear calibration ranges should be established for each analyte by determining the signal responses from a minimum of three concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined

whenever there is a significant change in instrument response and every six months for those analytes that periodically approach their linear limit.

12.4.1 For work following the Army Corp of Engineers Shell document, the linear range cannot exceed the level of the high calibration standard on that run. All elements to be reported that exceed the high standard must be reanalyzed on dilution and the results reported from the dilution.

12.5 Initial Calibration Verification Standard (ICV). After each calibration, a standard from a different source than the calibration standard should be analyzed with an initial calibration blank (ICB). For the ICV, all elements to be reported must be within 10 percent of the true value and the replicates exceed 5 times the reporting limit should have a relative standard deviation of < 5%. The ICB results should be less than three times the IDL or less than 1/10 of the concentration of the action level of interest. (All ICB values should be less than the reporting limits for the elements).

12.6 Interference Check Standard. An interference check standard must be analyzed at the beginning of each analytical run. For all spiked elements, the analyzed results must be within 20 percent of the true values. For unspiked elements, the interfering element solutions should contain less than the absolute value of two times the reporting limit for each element. If this criteria is not met, then no samples containing the elements in question can be reported in the area bracketed by this QC unless the samples contain no significant interferents. This method does not require the analysis of an interfering element check solution at the end of the run. However, this may be required due to meet other method and/or client requirements. Run the ICSA and ICSAB solutions every 8 hours unless otherwise instructed by the metals lab supervisor or manager.

12.7 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain elements at less than the reporting limit for each element. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

12.7.1 For work following the DOD program code, an acceptance criteria < 1/2 the RL must be applied.

12.8 Lab Control Sample/Spike Blank. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. For a running batch, a new lab control sample or spike blank is required for each different digestion day. The laboratory should assess laboratory performance of an aqueous lab control or spike blank against recovery limits of 80 to 120 percent. For solid lab controls, the elements should be within the range given by the lab control supplier. If the lab control or spike blank is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element.

12.9 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. The control limits

for the matrix spike recovery are from 75 to 125 percent recovery. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result)/Amount Spiked) x 100 = matrix spike recovery

12.9.1 Some clients may require a post-digest spike if the matrix spike is outside of the control limits. Spiking levels should be set as per client requirements. Either CLP type spike levels or SW846 spike levels may be used, depending on client needs. Check with the metals supervisor for more information.

12.9.1.1 For CLP type post-digest spikes, the sample should be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 75 to 125 percent are normally applied, unless a client specifies a different limit. No action is necessary if the post-digest spike is outside of this limit, unless a preparation problem is suspected with the spike, in which case the post-digest spike should be remade and reanalyzed. The post-digest spike recovery should be footnoted on the matrix spike recovery for the element of interest.

12.9.1.2 Method 6010B specifies that the post-digest spike be in the range of 10 to 100 times the detection limit. Limits of 75 to 125 percent are normally applied, unless a client specifies a different limit. No action is necessary if the post-digest spike is outside of this limit, unless a preparation problem is suspected with the spike, in which case the post-digest spike should be remade and reanalyzed. The post-digest spike recovery should be footnoted on the matrix spike recovery for the element of interest.

12.9.1.3 Work done under the DOD program code must follow DOD limits for matrix spikes. Refer to program code for specific instructions.

12.10 Matrix Spike Duplicate. The laboratory must digest a matrix spike duplicate sample for a minimum of 1 in 20 samples. A duplicate may be used in place of a matrix spike duplicate on client request. The relative percent difference (rpd) between the matrix spike and the matrix spike duplicate should be assessed. The matrix spike duplicate or duplicate rpd is calculated as shown below. The control limit for the duplicate is 20% rpd. If a matrix spike duplicate or duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

$$\frac{(|\text{Matrix Spike Result} - \text{Matrix Spike Duplicate Result}|) \times 100}{(\text{Matrix Spike Result} + \text{Matrix Spike Duplicate Result})/2} = \text{Duplicate RPD}$$

12.11 Continuing Calibration Verification. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample or every two hours during an

analysis run, whichever is more frequent, and at the end of the sample run. If the CCV solution is not within 10 percent of the true value and the relative standard deviation for the replicates greater than 5 times the reporting limit is not < 5%, then no samples can be reported in the area bracketed by the failing CCV. An exception is that if the recovery of the CCV is in the range of 111% to 125% and the sample results are less than the report limits. (Note: If a CCV fails due to a calibration shift, rather than a one time problem, then the instrument should be recalibrated and the QC rechecked before any additional samples are analyzed.)

12.11.1 If the CCV recovery is within specification and the relative standard deviation is high, then the CCV can be reanalyzed as long as the 10% frequency is met. If the reanalysis is within specifications, then the bracketed samples can be reported.

12.12 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample or every 2 hours during an analysis run, whichever is more frequent, and at the end of the sample run. The CCB results should be less than three times the IDL or less than 1/10 of the concentration of the action level of interest and less than the reporting limit. If the CCB does not meet this criterion and is less than the reporting limit, it can be reanalyzed two more times. The average of the three readings must be within 3 standard deviations of the background mean. If these criteria are not met, then no samples can be reported in the area bracketed by the failing CCB for the failing element. The exception is that samples that are less than the reporting limit may be reported if the CCB is biased high, but is still less than the reporting limit. If the initial CCB is above the reporting limit, then all samples should be submitted for reanalysis. Do not rerun the CCB if the initial reading is above the reporting limit. If reanalysis of the CCB is required, reanalyze a new pair of CCV, CCB before proceeding with the analysis of any additional samples.

12.12.1 For work following the DOD program code, the initial and continuing calibration blanks must be less than 2 times the MDL. Refer to section 12.2 for a definition of the MDL for this program.

12.13 Low Level Calibration Check (CRI). The CRI solution is run after the calibration is completed and before any samples are analyzed. Normal in house limits of 50 to 150 are applied to the CRI standard, but tighter criteria may be needed in some client or project specific situations.

12.13.1 For all samples, the CRI check solution must be at the reporting limit for each element. If special client reporting limits are requested, then low checks corresponding to those reporting limits must also be analyzed.

12.13.2 For MDL reporting, low checks are not required at the MDL, but the sample results must be flagged with the appropriate concentration qualifiers to indicate that the reported values are below the reporting limits, but above the MDL.

12.13.3 For work following the DOD program code, an acceptance criteria of 80 to 120 percent must be applied to all elements whose RL is greater than 3 times the MDL unless a project specific waiver is obtained.

12.14 Serial Dilution Analysis. For one sample per preparation batch, or whenever matrix interferences are suspected for a batch of samples, it is recommended that a serial dilution be prepared. For the serial dilution, a 1:5 dilution should be made on the sample. The results of the 1:5 dilution should agree within 10 percent of the true value as long as the sample and the dilution result are greater than 50 times the IDL. If the dilution does not agree, then remake and reanalyze the serial dilution. If the reanalysis is again not within the limit, the failing elements should be reported with a footnote indicating that there were possible matrix interferences. Alternatively, a serial dilution can be done with larger dilutions, and the sample can be reported from the dilutions. For example, a sample that failed the serial dilution criteria using the straight sample and a 1:5 dilution may pass the serial dilution criteria using a 1:2 dilution and a 1:10 dilution. In that case, the sample would be reported from the 1:2 dilution and the results would be footnoted that a dilution was required due to matrix interference. The calculation to be used for serial dilutions is shown below.

((Sample Result - Serial Dil. Result)/Sample Result) x 100 = Serial Dilution RPD

12.15 Post Digestion Spike Addition. Post-digest spikes may also be used to determine potential interferences. Check with the metals supervisor for further information on when a post-digest spike should be performed. Recovery limits of 75 to 125 percent should be used to assess post-digest spikes.

12.16 IEC Correction Factor Generation. All interfering element correction factors (IEC's), must be verified and updated a minimum of once every 6 months or whenever instrument conditions change significantly.

13.0 CALCULATIONS

13.1 For water samples, the following calculations should be used. Refer to the QC section for the calculations to be used for the QC samples.

original sample concentration of metal (µg/l) =

$$\frac{\text{(conc. in the digestate (µg/l)) x (final digestate volume (ml))}}{\text{(Initial sample volume (ml))}}$$

13.2 For soil samples, the following calculations should be used.

concentration of the metal in the dry sample (mg/kg) =

$$\frac{\text{(conc. in the digestate (mg/l) x final digestate volume(L))}}{\text{(sample wt. (kg)) x (\% solids/100)}}$$

14.0 DOCUMENTATION REQUIREMENTS

14.1 If any samples or QC checks require reanalysis, a brief explanation of the reason must be documented in the raw data. All instrument data should be exported to the LIMS system and a copy of the run log should be included in the logbook by the instrument.

14.2 The Standard Preparation Logbook must be completed for all standard preparations. All information requested must be completed. The Accutest Lot Number must be cross-referenced on the standard vial.

14.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. A copy of any outside maintenance reports should also be kept in the log. In addition to the maintenance, the maintenance log should also contain daily information on such items as the profile intensity. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

14.5 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

15.0 INSTRUMENT MAINTENANCE

15.1 Recommended periodic maintenance includes the items outlined below.

15.2 Change the pump tubing weekly or as needed.

15.3 Clean the filter on the recirculating pump approximately once a month and dust off the power supply vents every one to two weeks.

15.4 Clean the nebulizer, torch, and injector tube every two to four weeks or more often as needed.

15.5 Change the sampler tip as needed (every one to two months).

15.6 Clean the recirculating pump lines every 3 months or more often if needed.

15.7 Clean the slides on the autosampler with methanol and wipe them with a KimWipe saturated with Teflon spray a minimum of once per day.

15.8 For the TJA Trace, check and clean the filters every one to two weeks.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This

document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes

16.2.3 Chlorinated organic solvents

16.2.4 Non-chlorinated organic solvents

16.2.5 Hazardous solid wastes

16.2.6 Non-hazardous solid wastes

17.0 ADDITIONAL REFERENCES

17.1 Refer to other SOP's for ICP analysis.

17.2 Refer to Thermo instrumentation manuals.

TABLE 1: NORMAL REPORTING LIMITS BY ELEMENT			
Analyte	**Water & Wipe Reporting Limit (µg/l)**	**Soil Reporting Limit (mg/kg)**	**TCLP Reporting Limit (mg/l)**
Aluminum	200	20	
Antimony	6	2	
Arsenic	8	2	0.50
Barium	200	20	1.0
Beryllium	1	0.2	
Cadmium	3	0.5	0.005
Calcium	5000	500	
Chromium	10	1	0.010
Cobalt	50	5	
Copper	10	2.5	
Iron	100	10	
Lead	3	2	0.50
Magnesium	5000	500	
Manganese	15	1.5	
Nickel	10	4.0	
Potassium	10000	1000	
Selenium	10	2	0.50
Silver	10	0.5	0.010
Sodium	10000	1000	
Thallium	10	1	
Vanadium	50	5	
Zinc	20	2	
Boron	100	10	
Molybdenum	20	1	
Palladium	50	5.0	
Silicon	200	20	
Strontium	10	1	
Tin	10	5	
Titanium	10	1	

TABLE 2: ANALYTICAL LINES ON THE TJA TRACE3	
Element	**Wavelength**
Al	308.215
As	189.042
Ca	317.933
Fe	271.441
Mg	279.078
Mn	257.610
Pb	220.353(a)
Se	196.026(a)
Tl	190.864
V	292.402
Ag	328.068
Ba	493.409
Be	313.042
Cd	226.502
Co	228.616
Cr	267.716
Cu	324.753
K	404.720(b)
Na	330.232
Ni	231.604
Sb	206.838
Mo	202.030
Pd	340.458
Si	288.158
Sn	189.989
Zn	206.200

a. *This element has two lines at this wavelength so that Crawford-Kunselman Noise Reduction techniques can be applied.*
b. *This element has two wavelengths so that a broader linear range is available.*

TABLE 3: CALIBRATION STANDARD LEVELS in ug/L						
Element	**STD A (Blank)**	**STD B**	**STD C**	**STD D**	**STD E**	**STD F**
Ba	0	4000	NA	NA	NA	NA
Be	0	4000	NA	NA	NA	NA
Cd	0	4000	NA	NA	NA	NA
Cr	0	4000	NA	NA	NA	NA
As	0	4000	NA	NA	NA	NA
Se	0	4000	NA	NA	NA	NA
Pb	0	4000	NA	NA	NA	NA
Tl	0	4000	NA	NA	NA	NA
Mn	0	4000	NA	NA	NA	NA
Co	0	4000	NA	NA	NA	NA
Zn	0	4000	NA	NA	NA	NA
Cu	0	4000	NA	NA	NA	NA
Ni	0	4000	NA	NA	NA	NA
Sb	0	4000	NA	NA	NA	NA
Mo	0	4000	NA	NA	NA	NA
B	0	4000	NA	NA	NA	NA
Sn	0	4000	NA	NA	NA	NA
Ti	0	4000	NA	NA	NA	NA
Ag	0	500	NA	NA	NA	NA
V	0	4000	NA	NA	NA	NA
Sr	0	4000	NA	NA	NA	NA
Si	0	10000	NA	NA	NA	NA
Pd	0	4000	NA	NA	NA	NA
Al	0	(5000)	(20000)	(40000)	(60000)	80000
Ca	0	(5000)	(20000)	(40000)	(60000)	80000
Fe	0	(5000)	(20000)	(40000)	(60000)	80000
Mg	0	(5000)	(20000)	(40000)	(60000)	80000
K	0	(5000)	(20000)	(40000)	(60000)	80000
Na	0	(5000)	(20000)	(40000)	(60000)	80000

Note: Values in ( ) are optional, but may be included in the curve to provide a better linear fit. All fits must be first order.

TABLE 4: ICV, and CCV LEVELS		
Element	**ICV Suggested Level in ug/l**	**CCV Suggested Level in ug/l**
Al	5000	40000
As	1000	2000
Ca	5000	40000
Fe	5000	40000
Mg	5000	40000
Mn	1000	2000
Pb	1000	2000
Se	1000	2000
Tl	1000	2000
V	1000	2000
Ag	500	250
Ba	1000	2000
Be	1000	2000
Cd	1000	2000
Co	1000	2000
Cr	1000	2000
Cu	1000	2000
K	10000	40000
Na	10000	40000
Ni	1000	2000
Sb	1000	2000
Zn	1000	2000
B	1000	2000
Mo	1000	2000
Pd	1000	2000
Sr	1000	2000
Sn	1000	2000
Ti	1000	2000
Si	1000	5000

TABLE 5: SUGGESTED CONCENTRATIONS OF METALS IN THE MATRIX SPIKE AND SPIKE BLANK			
Element	**Soils Final Concentration in mg/kg**	**Aqueous Final Concentration in µg/l**	**TCLP Leachates Final Concentration in mg/l**
Ag	10	50	0.05
Al	5400	2000	
As	400	2000	2.0
B	100	2000	
Ba	400	2000	10.0
Be	10	50	
Ca	1250	25000	
Cd	10	50	0.05
Co	100	500	
Cr	40	200	0.20
Cu	50	250	
Fe	5200	1000	
K	1250	25000	
Mg	1250	25000	
Mn	100	500	
Mo	100	2000	
Na	1250	25000	
Ni	100	500	
Pb	100	500	2.0
Sb	100	500	
Se	400	2000	2.0
Tl	400	2000	
V	100	500	
Zn	100	500	
Sn	100	2000	
Sr	100	2000	
Ti	100	2000	
Si	200	4000	
Pd	100	2000	

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager: Wendy

QA Manager: Donna Huffman

Effective Date: 3/14/13

TITLE: **COLD VAPOR ANALYSIS OF MERCURY FOR WATER SAMPLES**

REFERENCE: EPA 245.1, revision 3.0 (1994) and SW846 7470A (modified)

Revised Sections: ***8.0, 8.4 (cancelled), 8.5 and 8.6 renumbered, 9.4, 9.8.2, 9.8.3, 10.2, 10.3, 10.4, 10.5, 10.6, Section 11 cancelled, Sections 12, 13, 14, 15, 16 and 17 renumbered.***

1.0 SCOPE AND APPLICATION

1.1 This method can be applied for the analysis of mercury for all potable and non-potable water samples. This SOP is based on the May 1994 revision of EPA method 245.1. The reporting limit for mercury water samples based on the procedures outlined in this SOP, is 0.0002 mg/l.

1.2 Aqueous wastewater may also be analyzed following method 7470A. The modification to this method are a direct scale-down of the reagents and the use of an automated analyzer.

2.0 SUMMARY

2.1 Cold vapor mercury is a flameless AA procedure based on the absorption of radiation at 253.7 by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Results are quantitated by comparison to a daily calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. The calibration check standard must be run at a frequency of 10 percent or less.
The mid-level calibration check standard criteria is either ± 5 or ± 10 percent of the true value.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.
Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house

limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{\text{(|MS Result - MSD Result|)} \times 100}{\text{(MS Result + MSD Result)/2}} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 After the mercury digestate is reduced to Hg vapor, it must be handled in a closed system or in a hood to prevent inhalation of the toxic vapor. Make sure that the Hg instrument is vented directly to a hood.

6.0 PRESERVATION AND HOLDING TIME

6.1 All water samples must be preserved by acidification with nitric acid to a pH of 2 or lower and stored in a polyethylene or glass container.

6.2 All samples must be analyzed within 28 days of the date of collection.

7.0 INTERFERENCES

7.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations of sulfide as sodium sulfide as high as 20 mg/l do not interfere with mercury recoveries when following this method. High copper concentrations (> 10 mg/l) may also interfere with mercury recoveries.

7.2 Samples that are high in chloride such as seawater, brine, and industrial effluent may require as much as 25 ml of additional permanganate. NOTE: When chloride concentrations are high, hydroxylamine sulfate and stannous sulfate should be used in place of the corresponding chlorides.

7.3 Finally, certain volatile organic materials will also absorb at this wavelength and can interfere. It can be determined if this type of interference is present by doing a preliminary run without reagents.

8.0 APPARATUS

8.1 Three Leeman instruments are available for analysis. **They are Leeman Hydra II** automated analyzers. Refer to the instrument manuals for further details on this instrumentation, including proper venting and safety requirements. Instrument maintenance is outlined below.

8.1.1 Change the sample tubing as needed.

8.1.2 Change the drying tubing as needed.

8.1.3 Clean the exterior of the instrument as needed.

8.1.4 Adjust the Hg lamp as needed. This can be done in the software on both instruments.

8.1.5 Complete any other maintenance required to maintain the instrument in good running order including, but not limited to, cleaning the cell, changing other tubing, changing the Hg lamp, etc.

8.2 Heating Equipment.

8.2.1 Graphite heating block. Capable of heating at 95 °C for 2 hours.

8.3 Digestion Bottles. Disposable plastic digestion tubes are used with the graphite heating block.

8.3.1 Disposable plastic digestion tubes (65 ml volume) with tops for graphite heating block.

8.4 Class A, to deliver, volumetric cylinders for measuring initial sample volumes and for calibrating glass tubes as outlined above.

8.5 Automatic pipettor bottles. Refer to EQA063 for calibration information.

9.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. All solutions listed below may be scaled up or down proportionally as needed.

9.1 Sulfuric acid, concentrated.

9.2 Nitric acid, concentrated. This acid must have a low mercury content.

9.3 Dilution acid. To approximately 400 ml of DI water, add 33.4 ml of concentrated sulfuric and 16.6 ml of concentrated nitric. Dilute to a final volume of 1000 ml. This dilution acid is used for making dilutions of digested samples.

9.4 Stannous chloride. Add 25 ml of concentrated hydrochloric acid to approximately 400 ml of DI water. Dilute to 500 ml with DI water and mix well. Add 50 g of stannous chloride dihydrate or 42 g of stannous chloride anhydrous and dissolve. Make sure that this solution is dissolved while in use.

9.4.1 Stannous sulfate may be used in place of stannous chloride.

9.5 Sodium chloride-Hydroxylamine hydrochloride. Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to 2000 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

9.6 Potassium Permanganate, 5 percent solution, w/v. Add 50 g of potassium permanganate to 1000 ml of water and mix well. **Caution** - Potassium permanganate is a strong oxidizing agent. Handle with care.

9.7 Potassium Persulfate, 5 percent solution, w/v. Dissolve 50.0 g of potassium persulfate in 1000 ml of water and mix well. **Caution** - Potassium persulfate is a strong oxidizing agent. Handle with care.

9.8 Mercury standard solutions.

9.8.1 10 ppm Hg solution. Using a 1.00 ml volumetric pipet or autopipet, add 1.00 ml of 1000 ppm stock (to be purchased from a vendor such as Fisher) to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with water and mix well. This standard may be held for up to 28 days.

9.8.1.1 The 10 ppm external source should be made up following the directions in 9.8.1.

9.8.2 **30.0** ppb Hg solution. Using an autopipet, add **0.300** ml of 10 ppm Hg solution to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

9.8.2.1 The 30.0 ppb external source should be made up following the directions in 9.8.2.

9.8.3 **3** ppb Hg solution. Using volumetric pipets or autopipets, add 10.0 ml of **30.0** ppb Hg solution to a 100 ml volumetric flask containing approximately 75 ml of DI water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

10.0 WATER DIGESTION FOR GRAPHITE HEATING BLOCK

Below is a step-by-step procedure for the digestion and analysis of water samples for mercury.

10.1 If necessary, acid rinse disposable digestion tubes with 10% nitric acid and deionized water before use.

10.2 Make up a standard curve consisting of 5 standards and a blank. Suggested concentrations are shown below. All standards are made up to a final volume of **30** ml. Different concentrations may also be used, as long as all of the method requirements are met. Make sure to clearly label each bottle. Calibration standards must be prepared fresh with each digestion batch.

ml of 3 ppb Hg solution	ml of 30 ppb Hg solution	Ml of DI water	Total ug of Hg	ug/L of Hg
0.000	0.000	**30**	0.000	0.000
2.00	0.000	**28.0**	**0.006**	0.20
5.00	0.000	**25.0**	**0.015**	0.50
0.00	1.00	**29.0**	**0.030**	1.00
0.00	2.50	**27.5**	**0.075**	2.50
0.00	5.00	**25.0**	**0.150**	5.00

10.3 Samples. For each sample, homogenize the sample well and pour out a representative aliquot of the sample into the digestion tube to the 30 ml mark. The digestion tubes are purchased from independent vendor and they are certified for the 50ml only. Accutest calibrates the 30ml volume for the 10% of the total tubes of any lot. The calibration results must be recorded in a log book with a QC/QA controlled book number. A smaller volume may be used if there are matrix problems or high levels of mercury in the sample using a class A, to deliver, graduated cylinder. .

10.4 Make up additional quality control samples as shown below, using a final volume of **30** ml for each check standard. (Note: if a different standard curve is run, then the levels of the CCV and ICV standards should be adjusted accordingly in accordance with the requirements in the methods) Make sure to clearly label each bottle. Make sure to prepare enough CCV checks for the entire run. The ICV check must be from an alternate source of standards than the calibration curve. The CCV must be made from the same source as the calibration curve. A low check standard at the level of the CRDL (0.20 ug/l) is also required. This 0.20 ug/l check can be made up as outlined for the standard curve.

Sample ID	ml of 30 ppb Hg solution	ml of DI water	Total ug of Hg
CCV Check(s)	2.5	27.5	**0.075**
MB	0.0	30	**0.0**
MS	2.0	(a)	**0.06 (b)**
MSD	2.0	(a)	**0.06 (b)**

ICV	3.0	**27.0**	**0.09**
LCS	2.0	**28.0**	**0.06**

(a) **30** ml of sample
(b) plus the level of Hg in the sample.

10.5 To all samples, QC, and standards add the reagents listed below, swirling the samples well after each addition of reagent. Allow the samples to stand for at least 15 minutes after the addition of the permanganate. If the sample decolorizes, add additional permanganate until the purple color persists.

- **1.5** ml of conc. sulfuric acid.
- **0.75** ml of conc. nitric acid.
- **4.0** ml of 5% permanganate solution.

Wait 15 minutes, then

- **2.4** ml of potassium persulfate solution.

10.5.1 All of the additions shown can be done with a bottle pipettor which must be accurate to within a range of 90 to 110%.

10.6 Cap the samples and place them in the graphite heating block and heat for 2 hours at **90 to** 95 °C. Record the digestion times and temperature.

10.7 Enter the prep data into the LIMS system, double checking all volumes and spike amounts. After the prep data is checked, it can be approved and is available for use in the final calculations.

11.0 COLD VAPOR ANALYSIS PROCEDURE HYDRA II

11.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operators' manual.

11.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

11.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

11.1.3 Turn on the analyzer and allow it to warm up.

11.1.3.1 For the Hydra AA II, open the Envoy software. Go to Method and click Instrument Control. On the Instrument Control page, click the startup icon. This will turn on the lamp, gas, and pump. You may

also turn on/off the lamp, gas and pump individually on the Instrument Control Page.

11.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not overtighten.

11.1.4.1 Go to the Instrument control tab and pick the gas control test option. The input should be approximately 0.25 LPM. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.5 Start a batch to save your data.

11.1.5.1 Create a new chapter (Data File) by clicking Analysis. The batch should normally be named H5 followed by the month date and year, followed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument for 3/24/03 would be named H5032411w1. The realtime print option can also be turned on from this tab.

11.1.5.2 Set up autosampler racks containing the samples that are going to be run.

11.1.5.3 Create a new sequence by clicking sequence-new. Type the sequence name. After typing the samples in to sequence page make sure to click update and save. CCV and CCB checks can be entered in the macro column of the sequence page.

11.1.6 Set up the calibration.

11.1.6.1 Go to the Method menu, enter or verify the standard concentration by clicking on the standard tab. Also select number of replicates to be run for each standard. Normally one replicate is run per standard. The check standard concentrations and acceptance ranges are also defined under this standard info tab. Make sure to always click apply when any changes are made in a tab.

11.2 Add hydroxylamine hydrochloride to all samples and standards as outlined below.

12.2.1 Add **1.8** ml of hydroxylamine hydrochloride solution to each standard and sample and swirl until the solution has been completely decolorized. Transfer to a calibrated glass cylinder and dilute to a final volume of **50** ml and swirl to mix.

12.2.2 They hydroxylamine hydrochloride can be added using a bottle pipettor which is accurate in a range of 90 to 110%.

11.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride

bottle.

11.4 Start the calibration.

12.4.1 Click run sequence. The instrument will run the calibration and then pause. Click stop. Go to the Calibration page. Accept the calibration and then print the calibration. Click the Document icon, then choose HG5-PDF. Rename the file as MA*****_cal.

11.5 After the calibration has been accepted, start to run the samples.

12.5.1 For the Hydra AA II, go to the Sequence page. Right click on the first sample (ie. ICV) and click start from here.

11.6 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see Section 9.3) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

11.7 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports should be transferred into the LIMS system where the final calculations are done.

12.7.1 Go to analysis-Click result-Click chapter. Then go to report and select report spec. The normal report spec is "ACCUTEST". Click OK. Click on chapter in order to select all samples. Then click report output and then csv.file. Save as MA*****.csv. To print, select printer output and then type the report title (i.e. MA*****) and enter OK.

11.8 The calculations are done in the LIMS as described below. A final volume of 40.0 ml is used for calculation purposes for graphite heating block digestions. (The volume of 60.0 ml is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 40.0 ml.)

Final sample concentration in mg/L =

$$\frac{\text{concentration in the digestate in ug/l x final volume in ml}}{\text{Initial volume in ml}}$$

11.9 Review the data in the LIMS, adding comments and accepting results as appropriate.

11.10 Shut down the instruments.

12.10.2 To shut down the Hydra AA II, move the stannous chloride line from the stannous chloride bottle to the 10% HNO3 rinse bottle. Let the system rinse with 10% HNO3 for several minutes. Then switch the line to DI water bottle and let rinse for several more minutes. Let the pump and gas run until the lines are completely dry. Then go to instrument control menu and click off icon for Lamp, Gas and Pump.

12.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

12.1 Instrument Detection Limits (IDLs). The instrument detection limits must be done a minimum of once per year or when instrument conditions change significantly. The IDL is generated by running 10 replicates of a digested blank. The IDL is then defined as 3 times the standard deviation of the 10 replicates of the blank.

12.2 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.143, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

12.3 Instrument Calibration. The instrument must be calibrated daily or at a minimum of once every 24 hours and each time the instrument is set up. Calibration standards should be prepared fresh with each preparation batch. A minimum of a blank and 5 standards are required. The correlation coefficient of the curve must be a minimum of 0.995. No samples should be analyzed until all of the calibration criteria are met. Resloping is acceptable as long as it is immediately preceded and immediately followed by a complaint CCV and CCB.

12.4 Linear Dynamic Range (LDR). For each instrument, the upper limit of the linear dynamic range must be established. A linear calibration should be prepared from 3 standards, one of which is close to the upper limit of the linear range. The LDR is determined by analyzing succeedingly higher standard concentrations of mercury until the observed analyte concentration is no more than 10 percent below the true value of the standard. Sample concentrations that are greater than 90% of the determined upper LDR limit must be analyzed using dilutions. The LDR should be verified annually or whenever there is a significant change in the instruments analytical performance.

12.5 Quality Control Sample (also referred to as Initial Calibration Verification Standard (ICV)). At a minimum of once per quarter, a standard from a different source than the calibration standard must be analyzed. Normally this is analyzed at the beginning of the run <u>after</u> the CCV and CCB checks. The ICV must be within 10 percent of the true value. It is recommended that this standard be analyzed with each run so that it is included with all client reports. For SW846 7470A, this standard should be at a concentration near the midpoint of the calibration curve. If the ICV is outside of the acceptance limits, then the problem must be corrected and the ICV reanalyzed and shown to be within QC limits before any samples can be reported. All reported samples must be bracketed by an ICV which meets acceptance criteria.

12.5.1 If the ICV is biased high and all sample results are < RL, then, at the

discretion of the data reviewer, data may be reported.

12.6 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. The method blank must contain mercury at less that the reporting limit. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

12.7 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample (spike blank) with each set of samples. A minimum of one lab control sample is required for every 20 samples. For a running batch, a new lab control sample is required for each different digestion day. For method 245.1, the laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 85 to 115 percent. For method 7470A, the laboratory must assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120 percent. In either case, if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag. If the lab control recovery is low or there are samples above the reporting limit, then all affected samples must be redigested and reanalyzed.

12.8 Matrix Spike.

12.8.1 For method 245.1, the laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The spike recovery should be within the limits of 70 to 130. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

12.8.2 For method 7470A, the laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The laboratory should assess the matrix spike recovery against limits of 75 to 125. (In house control limits are also generated on an annual basis and are used to support the default limits.) An exception to this rule occurs where the sample concentration exceeds the spike concentration by a factor of 4 or more. If the matrix spike fails this criterion, then the sample should be flagged as showing possible matrix interferences.

12.8.3 Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculation shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

12.9 Matrix Spike Duplicate or Matrix Duplicate. The laboratory must digest a matrix spike

duplicate or a duplicate sample for a minimum of 1 in 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. The relative percent difference (rpd) between the matrix spike duplicate and the matrix spike or between the duplicate and the sample should be assessed. The calculations for both rpds are shown below.

12.9.1 For method 245.1, the control limits for the matrix spike duplicates or the duplicates are calculated on an annual basis and are used to assess whether a matrix spike duplicate or a duplicate is in control. If it is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

12.9.2 For method 7470A, the duplicate or matrix spike duplicate RPD must be assessed against a limit of 20% RPD. (In house control limits are also generated on an annual basis and are used to support the default limits.) If it is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

12.9.3 Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero. Refer to the calculations shown below.

$$\frac{(\text{Sample Result - Duplicate Result}) \times 100}{(\text{Sample Result + Duplicate Result}) \times 0.5} = \%\ \text{RPD}$$

or

$$\frac{(|\text{MS Result - MSD Result}|) \times 100}{(\text{MS Result + MSD Result})/2} = \text{MSD RPD}$$

12.10 Continuing Calibration Verification. (Also known as the instrument performance check solution.) The CCV must be from the same source as the calibration curve.

12.10.1 Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within a method specified range of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentration should be at or near the mid-range of the calibration curve.

12.10.1.1 For method 245.1, the CCV must be within 10 percent of the true value.

12.10.1.2 For method 7470A, the CCV must be within 20 percent of the true

value.

12.10.2 The ICCV check must also be analyzed at the beginning of the run, immediately after the instrument is calibrated. For method 245.1, this first check must be within 5 percent of the true value. If it is not and there is not a problem with the standard solution, the instrument should be recalibrated and rechecked.

13.10.2.1 This check is not required for method SW846 7470A.

12.11 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

12.12 CRA (Low) Check. For all runs, a low check at the level of the CRDL (0.20 ug/l) or reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. No specific acceptance criteria are listed in any of the methods for this standard at this time. An in-house criterion of 50 to 150% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

12.12.1 If the CRA is biased high and there is no mercury found in the samples, then the sample results may be reported for mercury. If the CRA is biased high and there is mercury found in the samples, then the samples with Hg at levels ranging from the CCV to the high standard may be reported. Samples with levels of mercury between the CRA and the CCV standard may be biased high and cannot be reported.

12.12.2 Some client may require additional bracketing low checks to be analyzed. Client specific limits may also be required. Check with the area supervisor or manager for more information.

13.0 DOCUMENTATION REQUIREMENTS

Refer to the laboratory Quality Assurance Manual for additional documentation requirements.

13.1 Sample Worksheets. Digestion data sheets for the Hg water samples must show all digestion information including the sample ID's, sample volumes, bottle numbers, start times, end times, and pressure or temperature, as appropriate for all digestions. The digestion method (i.e digestion block) must be indicated on the digestion sheet. All sample information should be clearly entered on these sheets. In addition, any unusual characteristics of the samples or the digestion procedure should be noted in the Comments sections. Make sure also that all dilutions are clearly documented.

13.2 Standards and Reagents. All stocks and reagents must be recorded in the reagent logbook. All standards should be recorded on the digestion log with the samples.

13.3 Any run comments should be written on the raw data for the analysis and on the run log in the LIMS.

13.4 Annual bottle calibration verifications must be documented in the Mercury Bottle calibration log.

14.0 DATA REVIEW AND REPORTING

14.1 All samples should be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for making sure that the raw data is fully documented and it is loaded into the LIMS system. They are responsible for submitting samples for redigestion and reanalysis, when appropriate.

14.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The reviewer is also responsible for making sure that the QC calculations are done correctly and that appropriate flags are added.

14.3 After the reviewer completes their review, the data is released for client access in the LIMS. The raw data and the run log are submitted to the area manager. The manager periodically does an additional review on data for technical completeness. Any hardcopy raw data is transferred to the report generation department for scanning and storage. Instrument data is transferred electronically.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS 004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes.

15.2.3 Chlorinated organic solvents.

15.2.4 Non-chlorinated organic solvents.

15.2.5 Hazardous solid wastes.

15.2.6 Non hazardous aqueous wastes.

16.0 ADDITIONAL REFERENCES

16.1 Leeman Hydra II instrument manual.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager Henry Cole

QA Manager

Effective Date: 5/21/12

TITLE: COLD VAPOR ANALYSIS OF MERCURY FOR SOIL SAMPLES

REFERENCES: SW846 7471B

Revised Sections: *7.1*

1.0 SCOPE AND APPLICATION

1.1 This method can be applied for the analysis of mercury in soils, sediments, bottom deposits, and sludge type materials. The reporting limit for mercury soil samples, based on a 0.6 g sample size, is 0.033 mg/kg.

2.0 SUMMARY

2.1 Cold vapor mercury is a flameless AA procedure based on the absorption of radiation at 253.7 by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Results are quantitated by comparison to a daily calibration curve.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve. Detected concentrations below this concentration cannot be reported without qualification.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. Recovery requirements vary by method. For this method a recovery from

80 to 120% is required. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's)

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation.

LOWER LIMIT OF QUANTITATION CHECK (also referred to as CRI, CRA, or LLQC). For all runs, a low check at the level of the reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. A method criterion of 50 to 150% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 After the mercury digestate is reduced to Hg vapor, it must be handled in a closed system or in a hood to prevent inhalation of the toxic vapor. Make sure that the Hg instrument is vented directly to a hood.

6.0 PRESERVATION AND HOLDING TIME

6.1 All solid samples should be stored at 4 ± 2°C until the time of digestion.

6.2 All samples should be analyzed within 28 days of the date of sampling.

7.0 APPARATUS

7.1 Three Leeman instruments are available for analysis. Two are Leeman Hydra II AA automated analyzers and the other is a Leeman Hydra AA automated analyzer. Refer to the instrument manuals for further details on this instrumentation, including proper venting and safety requirements. Instrument maintenance is outlined below.

7.1.1 Change the sample tubing as needed.

7.1.2 Change the drying tubing as needed.

7.1.3 Clean the exterior of the instrument as needed.

7.1.4 Adjust the Hg lamp as needed. This can be done in the software on both instruments.

7.1.5 Complete any other maintenance required to maintain the instrument in good running order including, but not limited to, cleaning the cell, changing other tubing, changing the Hg lamp, etc.

7.2 Graphite heating block. Capable of heating at 95 ± 3 °C for 2 hours.

7.3 Digestion Bottles . Disposable plastic digestion tubes (65 ml volume) with tops for graphite heating block.

7.4 Calibrated glass tubes with verified 60.0 ml and 100.0 ml final volume calibration mark for bringing graphite heating block digestates to their final volume. (The 60.0 ml calibration is only required for water digestions).

7.4.1 At a minimum of once per year, the calibration of these bottles must be verified and documented in the Hg Bottle calibration log following the procedure outlined below.

7.4.2 Carefully measure 60.0 ml of room temperature (20 to 25 deg. C) deionized water with a class A to deliver volumetric cylinder and pour into the calibrated Hg bottle.

7.4.3 If the bottom of the meniscus is on the calibration line, then the bottle passes calibration and can be used.

7.4.4 If the bottom of the meniscus is not on the line, then the bottle should be removed from service and replaced with a newly calibrated bottle. New bottles are calibrated following the same procedure as above, except that a line must be etched into the bottle at the bottom of the meniscus of the 60 ml of DI water.

7.4.4.1 Two different lines for the same volume (i.e. 60 ml) cannot be etched on the same bottle as that may lead to confusion in the measurement of the final volume.

7.4.5 Repeat the steps in 7.4.2 through 7.4.4 using a 100 ml final volume instead of the 60 ml final volume.

7.5 Class A , to deliver, volumetric cylinders for measuring initial sample volumes and for calibrating glass tubes as outlined above.

7.6 Analytical Balance, 4 place. Calibration must be verified daily before use with NIST traceable weights.

7.7 Automatic pipettor bottles. The calibration on these bottles must be verified as outlined in EQA063.

7.8 Volumetric pipets, class A.

8.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. All solutions listed below may be scaled up or down proportionally as needed. Different reagents are required for the different heating techniques.

8.1 Digestion Block Reagents.

8.1.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated nitric.

8.1.1.1 Make sure to only prepare the amount of acid that will be needed for the prep and analysis.

8.1.1.2 This preparation must be done in a hood.

8.1.2 Dilution Acid: To approximately 800 ml of DI water, add 37.5 ml of concentrated HCl and 12.5 ml of concentrated nitric acid. Dilute to 1000 ml with DI water and mix well. This dilution acid is used for making dilutions of digested samples from the digestion block digestion procedures.

8.1.3 Potassium permanganate, 5% solution: Dissolve 50 g of potassium permanganate in 1000 ml of DI water. **Caution** - Potassium permanganate is a strong oxidizing agent. Handle with care.

8.1.4 Stannous chloride. Add 7.5 ml of concentrated sulfuric acid to approximately 400 ml of DI water. Dilute to 500 ml with DI water and mix well. Add 50 g of stannous chloride and dissolve. Make sure that this solution is dissolved while in use.

8.1.4.1 Stannous sulfate may be used in place of stannous chloride.

8.1.4.2 If clogging occurs during analysis using the automated analyzer, then a less concentrated solution may be used.

8.1.5 Sodium chloride-Hydroxylamine hydrochloride or Sodium chloride-Hydroxylamine hydrosulfate. Add 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride to 2000 ml of water. Mix well. Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

8.2 Mercury standard solutions.

8.2.1 10 ppm Hg solution. Using a 1.00 ml volumetric pipette, add 1.00 ml of 1000 ppm stock (to be purchased from a vendor such as Fisher) to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with water and mix well. This standard may be held for up to 28 days.

8.2.1.1 The 10 ppm external source should be made up using a different mercury stock, and following the directions in 8.2.1.

8.2.2 100 ppb Hg solution. Using a 1.00 ml volumetric pipette, add 1.00 ml of 10 ppm Hg solution to a 100 ml volumetric flask containing approximately 75 ml of water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

8.2.2.1 The 100 ppb external source should be made up following the directions in 8.2.2.

8.2.3 10 ppb Hg solution. Using a 10.0 ml volumetric pipette, add 10.0 ml of 100 ppb Hg solution to a 100 ml volumetric flask containing approximately 75 ml of DI water and 2.0 ml of concentrated nitric acid. Dilute to volume with deionized water and mix well. This standard must be made fresh daily.

9.0 INTERFERENCES

9.1 Potassium permanganate is added to eliminate possible sulfide interferences. Concentrations as high as 20 mg/kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water. High copper concentrations (> 10 mg/kg) may also interfere with mercury recoveries.

9.2 Samples that are high in chlorides may require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 254 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and analyzed. This may be accomplished by using an excess of the hydroxylamine hydrosulfate.

9.3 Certain volatile organics may also absorb at this wavelength and can interfere.

10.0 GRAPHITE DIGESTION BLOCK PROCEDURE FOR SOIL DIGESTION

10.1 Make up a standard curve consisting of 5 standards and a blank. Suggested concentrations are shown below. Different concentrations may also be used, as long as all of the method requirements are met. Make sure to clearly label each digestion tube. Calibration standards must be prepared fresh each day. Add 5 ml of DI water to each standard before digestion. The final concentration of Hg is calculated in the final digestate.

Ml of 10 ppb Hg solution	ml of 100 ppb Hg solution	Total ug of Hg	ug/L of Hg
0.000	0.000	0.000	0.000
2.00	0.000	0.020	0.20
5.00	0.000	0.050	0.50
0.00	1.00	0.100	1.00
0.00	2.50	0.250	2.50
0.00	5.00	0.500	5.00

10.2 Samples. For each sample, homogenize the sample well and weigh out a 0.5 to 0.6 g aliquot of the sample into one labeled digestion tube. A solid lab control should be prepared in the same manner.

10.3 Make up additional quality control samples as shown below. (Note: if a different standard curve is run, then the levels of the CCV and ICV standards should be adjusted accordingly in accordance with the requirements in the method.) Make sure to clearly label each digestion tube. Make sure to prepare enough CCV checks for the entire run. The ICV check must be from an alternate source of standards than the calibration curve and at a different level than the CCV or the calibration standards. A low check standard is also required. This 0.20 ug/l check can be made up as outlined for the standard curve.

Sample ID	ml of 100 ppb Hg solution	ml of DIwater	µg/l of Hg
CCV Check(s)	2.5	7.5	2.5
MB	0.0	10.0	0.0
MS	2.0	0.0	2.0
MSD	2.0	0.0	2.0
Duplicate*	0.0	0.0	0.0
ICV	3.0	7.0	3.0

*Per project specification.

10.4 To all samples, QC, and standards add 5 ml of DI water and 5 ml of aqua regia and then heat for 2 minutes in a digestion block at 95 ± 3 °C. These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

10.5 Cool the samples and then add 25 ml of DI water and 15 ml of potassium permanganate solution to each sample and mix thoroughly. Allow the samples to stand for at least 15 minutes after the addition of the permanganate. If the sample decolorizes, add additional permanganate until the purple color persists.

10.5.1 These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

10.5.2 For samples containing a mixture of solvent and water, take a sample aliquot of approximately 20 g (lower for higher solvent samples) of sample and add the reagents listed above. Pour the sample in a beaker and heat on a hot plate at 95 ± 3 °C until no solvent layer is visible. Then transfer the digestate to a digestion tube and proceed as outlined below. A method blank and spike blank must also be taken through this entire procedure.

10.6 Cap the samples and place them in the graphite digestion block for 30 minutes at 95 ± 3 °C. Record the temperature and time for each digestion batch on the analysis sheet. Remove and cool.

10.7 Enter the prep data into the LIMS system, double checking all weights and spike amounts. After the prep data is checked, it can be approved and is available for use in the final calculation.

11.0 MERCURY ANALYSIS PROCEDURE HYDRA AA

11.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operators manual.

11.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

11.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

11.1.3 Turn on the analyzer and allow it to warm up.

11.1.3.1 In the software, go to the Runner section and select the control tab. Click on the Hg lamp and the pump. The gas will turn on automatically when the pump is turned off. If can also be turned on separately if necessary. The pump rates and gas pressure are set in the protocol. Refer to the instrument maintenance manual for more information on setting up a new protocol. If the

Hg lamp needs to be optimized, it can be done using the lab adjust on this page.

11.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not overtighten.

11.1.5 In the software, go to the Utility tab and pick the gas control test option. The output should be approximately 7 psi and the input should be between 60 to 90 psi. If the pressures are not correct, check with the area supervisor or manager before proceeding.

11.1.6 Start a batch to save your data.

11.1.6.1 Go to the sample runner tab and click on start new batch. The batch name is limited to 8 characters. The batch should normally be named H1 or H2 followed by the month and date, followed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument 2 for 3/24/03 would be named H20324w1. The realtime print option can also be turned on from this tab.

11.1.7 Set up autosampler racks containing the samples that are going to be run.

11.1.7.1 Go to main tab and click on the rack editor button. Enter your samples and the appropriate QC. CCV and CCB checks can be entered in the macro column. This tab may also be reached by clicking on the autosampler icon at the top of the page.

11.1.8 Set up the calibration.

11.1.8.1 Enter or verify the standard values. From the runner menu click on the standard tab. Click the buttons to the left of the standards that are to be run. Also click on the number of replicates to be run for each standard. Normally one replicate is run per standard. The standard concentrations are defined under the database menu under the line info tab. The check standard concentrations and acceptance ranges are also defined under this line info tab. Make sure to always click apply when any changes are made in a tab.

11.2 Finish the preparation of the samples and standards as outlined below.

11.2.1 For samples that were digested in the water bath or the graphite digestion block, add 6 ml of hydoxylamine hydrochloride or hydroxylamine hydrosulfate to each sample and standard and mix well. Transfer the entire digestate to a calibrated glass tube. Rinse the digestion tube 3 times with approximately 10 ml aliquots of DI water and add them to the digestate in the calibrated glass tube. Then bring the sample to a final volume of 100 ml with DI water and mix well.

11.2.1.1 These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

11.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

11.4 Start the calibration.

11.4.1 Turn on the real time report by checking the real time printing option on the runner menu either under main or under sample. Then go to the runner menu and the standard tab. Push the standard auto button. The calibration curve will be run by the autosampler. When the curve is complete, go to the database menu and click the calibration curve tab. Check to make sure that all acceptance criteria are met and then accept the curve. See section 13.3 for calibration curve criteria. Make sure that the curve is printed as soon as it is accepted.

11.5 After the calibration has been accepted, start to run the samples.

11.5.1 Go to the runner menu and the sample tab. Pick the autosampler rack that is to be run and type in the start cup and the end cup. Then push the button for run auto.

11.5.2 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see 8.1.2) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

11.6 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports should be transferred into the LIMS system where the final calculations are done.

11.6.1 Go to the data base menu and pick the report tab. Make sure that the correct report specification has been chosen (normally Accutest). Pick the batch that is to be printed and then push the generate report button. Generate both the electronic reports (prn file) and printed reports (report) from this menu.

11.7 The calculations are done in the LIMS as described below. . For soils, the calculation shown below is used. A final volume of 100 ml is used for calculation purposes. (The final volume is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 100 ml.)

$$\text{Final sample concentration in mg/kg} = \frac{\text{concentration in the digestate in ug/l x final volume}}{\text{Initial weight in g x (\%solids/100)}}$$

11.8 Review the data in the LIMS, adding comments and accepting results as appropriate.

11.9 Shut down the instruments.

11.9.1 To shut down the Hydra AA instrument, move the stannous chloride line from the stannous chloride bottle to the rinse container. Let the system rinse with 10% nitric for several minutes. Then switch the bath to DI water and let rinse for several more

minutes. Then empty the rinse bath and let the pump and gas run until the lines are completely dry. Go to Taskmaster and select the standby mode option. Release the tension on all of the pump clamps.

12.0 MERCURY ANALYSIS PROCEDURE HYDRA AA II

12.1 While the samples are digesting, begin setting up the Leeman analyzer following the steps outlined below. Additional instructions are available in the instrument operators manual.

12.1.1 Turn on the nitrogen and adjust to 60 to 90 psi. Turn on the instrument power if it is not already on.

12.1.2 Check the pump tubing and make sure that it is not flattened. Change if appropriate. Put the tubing in the clamps on the pump. Check the drying line and make sure that it is clean. Put fresh stannous chloride solution in the stannous chloride bottle. Fill the rinse bath or rinse bottle with fresh 10% nitric acid. The bath should be filled no more than ¾ full. Place the autosampler line and the stannous chloride line in the rinse container.

12.1.3 Turn on the analyzer and allow it to warm up.

12.1.3.1 Open the Envoy software. Go to Method and click Instrument Control. On the Instrument Control page, click the startup icon. This will turn on the lamp, gas, and pump. You may also turn on/off the lamp, gas and pump individually on the Instrument Control Page.

12.1.4 Tighten the pump clamps until the flow is coming evenly through the lines. Do not overtighten.

12.1.5 Go to the Instrument control tab and pick the gas control test option. The input should be approximately 0.25 LPM. If the pressures are not correct, check with the area supervisor or manager before proceeding.

12.1.6 Start a batch to save your data.

12.1.6.1 Create a new chapter (Data File) by clicking Analysis. The batch should normally be named H5 followed by the month date and year, followed by the matrix designation for the batch, following by the run number. For example, the first water batch on instrument for 3/24/03 would be named H5032411w1. The realtime print option can also be turned on from this tab.

12.1.7 Set up autosampler racks containing the samples that are going to be run.

12.1.7.1 Create a new sequence by clicking sequence-new. Type the sequence name. After typing the samples in to sequence page make sure to click update and save. CCV and CCB checks can be entered in the macro column of the sequence page.

12.1.8 Set up the calibration.

12.1.8.1 For the Hydra AA II, go to the Method menu, enter or verify the standard concentration by clicking on the standard tab. Also select number of replicates to be run for each standard. Normally one replicate is run per standard. The check standard concentrations and acceptance ranges are also defined under this standard info tab. Make sure to always click apply when any changes are made in a tab.

12.2 Finish the preparation of the samples and standards as outlined below.

12.2.1 For samples that were digested in the water bath or the graphite digestion block, add 6 ml of hydoxylamine hydrochloride or hydroxylamine hydrosulfate to each sample and standard and mix well. Transfer the entire digestate to a calibrated glass tube. Rinse the digestion tube 3 times with approximately 10 ml aliquots of DI water and add them to the digestate in the calibrated glass tube. Then bring the sample to a final volume of 100 ml with DI water and mix well.

12.2.1.1 These reagents can be added with a bottle pipettor that is accurate to within 90 to 110%.

12.3 Measure out aliquots of the digested standards and samples into the autosampler cups. Work from the prep log and double check all transfers. Let all samples sit uncovered in the open autosampler vials for a minimum of one minute. Place the racks in the autosampler. Move the stannous chloride line into the stannous chloride bottle.

12.4 Start the calibration.

12.4.1 Click run sequence. The instrument will run the calibration and then pause. Click stop. Go to the Calibration page. Accept the calibration and then print the calibration. Click the Document icon, then choose HG5-PDF. Rename the file as MA*****_cal.

12.5 After the calibration has been accepted, start to run the samples.

12.5.1 For the Hydra AA II, go to the Sequence page. Right click on the first sample (i.e. ICV) and click start from here.

12.5.2 Review the data. Any samples that are over the range of the curve should be diluted with the dilution acid (see 8.1.2) and reanalyzed. It is recommended that any sample analyzed after a sample with a value over the curve be reanalyzed for confirmation. Make sure to bracket every 10 samples with CCV and CCB checks.

12.6 Both paper and electronic reports can be generated using the report option. Never delete any samples from the reports. Electronic reports should be transferred into the LIMS system where the final calculations are done.

12.6.1 Go to analysis-Click result-Click chapter. Then go to report and select report spec. The normal report spec is "ACCUTEST". Click OK. Click on chapter in order to select all samples. Then click report output and then csv.file. Save as MA*****.csv. To print, select printer output and then type the report title (i.e. MA*****) and enter OK.

12.7 The calculations are done in the LIMS as described below. . For soils, the calculation shown below is used. A final volume of 100 ml is used for calculation purposes. (The final volume is factored out since all standards and samples are brought up to the same final volume and standard concentrations are calculated based on 100 ml.)

$$\text{Final sample concentration in mg/kg} = \frac{\text{concentration in the digestate in ug/l x final volume}}{\text{Initial weight in g x (\%solids/100)}}$$

12.8 Review the data in the LIMS, adding comments and accepting results as appropriate.

12.9 Shut down the instruments.

12.9.1 To shut down the Hydra AA II, move the stannous chloride line from the stannous chloride bottle to the 10% HNO3 rinse bottle. Let the system rinse with 10% HNO3 for several minutes. Then switch the line to DI water bottle and let rinse for several more minutes. Let the pump and gas run until the lines are completely dry. Then go to instrument control menu and click off icon for Lamp, Gas and Pump.

13.0 QUALITY CONTROL

Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

13.1 Instrument Detection Limits (IDLs). The instrument detection limits are determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of 7 consecutive replicates of a standard solution at a concentration from 3 to 5 times the estimated detection limit. IDLs must be done quarterly (every 3 months) for each instrument.

13.2 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.143, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response.

13.3 Instrument Calibration. The instrument must be calibrated daily or at a minimum of once every 24 hours and each time the instrument is set up. Calibration standards must be digested using the same procedure as the samples. A minimum of a blank and 5 standards are required. The correlation coefficient of the curve must be a minimum of 0.995. No samples should be analyzed until all of the calibration criteria are met.

13.3.1 A linear calibration using the equation $y = mx + b$ is applied where m is the slope and b is the intercept. The calibration is not forced through zero.

13.3.2 The correlation coefficient is calculated using the following equation:

$$Correl(X,Y) = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}}$$

where x is the measured absorbance and y is the standard concentration.

13.3.3 If the calibration curve does not meet criteria, and is redigestion, then any samples digested along with that calibration curve must also be redigested.

13.4 Initial Calibration Verification Standard (ICV)). During each analysis, a standard from a different source than the calibration standard should be analyzed. Normally this is analyzed at the beginning of the run. For this method, the ICV should be within 10 percent of the true value. When the measurements exceed these control limits, the analysis shall be terminated, and the problem corrected before proceeding. All reported results must be bracketed by compliant QC. The exception is, if the ICV is biased high (110 to 150 % recovery) and no mercury is found in the samples, then the sample results may be reported for mercury.

13.5 Continuing Calibration Verification. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCV solution is not within 20 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.)

13.6 Continuing Calibration Blank. Analyze the continuing calibration verification solution and the continuing calibration blank after every tenth sample and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

13.7 CRA (Low) Check or LLQC (Lower Limit of Quantitation Check). For all runs, a low check at the level of the reporting limit must be analyzed at the beginning of the run before analyzing any samples, but not before the ICV. A criterion of 50 to 150% recovery is applied to this low check standard. If this criterion is not met, then all samples associated with this CRA check must be reanalyzed along with a compliant CRA check.

13.7.1 A number of clients have specific program requirements for frequency and recovery ranges on CRA checks. Check with the metals supervisor for additional information on these programs.

13.7.2 If the CRA is biased high and there is no mercury found in the samples, then the sample results may be reported for mercury. If the CRA is biased high and there is mercury found in the samples, then the samples with Hg at levels ranging from the CCV to the high standard may be reported. Samples with levels of mercury between the CRA and the CCV standard may be biased high and cannot be reported.

13.8 Method Blank. The laboratory must digest and analyze a method blank with each batch of 20 samples. A minimum of one method blank is required for every 20 samples. A sample batch is defined as a maximum of 20 field samples in a preparation batch over a time period of 24 hours. A matrix spike/matrix spike duplicate, matrix spikes and/or duplicate is required

every 20 samples. The method blank must contain mercury at less that the reporting limit. If the method blank contains over that limit, the samples must be redigested or reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

13.9 Lab Control Sample. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control or spike blank is required for every 20 samples. Note: For soils, if a lab control is not available, a spike blank can be used. For a running batch, a new lab control sample is required for each different digestion day. The laboratory should assess laboratory performance of an aqueous lab control against recovery limits of 80 to 120%. In house lab control limits may also be generated to support these default limits. For solid lab controls, the elements should be within the range given by the lab control supplier. If the lab control is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

13.10 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. The laboratory should assess the matrix spike recovery against control limits of 80 to 120. (In house control limits are generated annually for information purposes only.). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

((Spiked Sample Result - Sample Result)/Amount Spiked) x 100 = matrix spike recovery

13.11 Matrix Spike Duplicate or Matrix Duplicate. The laboratory must digest a matrix spike duplicate or a duplicate sample for a minimum of 1 in 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. The relative percent difference (rpd) between the matrix spike duplicate and the matrix spike or between the duplicate and the original sample should be assessed. The rpds are calculated as shown below and should be assessed against a limit of 20% RPD. (In house control limits are generated annually for information purposes only.). If a matrix spike duplicate or a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

$$\frac{\text{(Sample Result - Duplicate Result) x 100}}{\text{(Sample Result + Duplicate Result) x 0.5}} = \text{\% RPD}$$

or

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

14.0 DOCUMENTATION REQUIREMENTS

Refer to the laboratory Quality Assurance Manual for additional documentation requirements.

14.1 Sample Worksheets. Digestion data sheets for the Hg soil samples must show all digestion information including the sample ID's, sample weights, bottle numbers, type of heating used, start times, end times, and pressure or temperature, as appropriate for all digestions. All sample information should be clearly entered on these sheets. In addition, any unusual characteristics of the samples or the digestion procedure should be noted in the comments sections. Make sure also that all dilutions are clearly documented.

14.2 Make sure to record thermometer ID, correction factor, and corrected and uncorrected temperatures for all temperature measurements.

14.3 Standards and Reagents. All stocks and reagents must be recorded in the reagent log book. All standards should be recorded on the digestion log with the samples.

14.4 Any run comments should be written on the raw data for the analysis and on the run log in the LIMS.

14.5 Annual bottle calibration verifications must be documented in the Mercury Bottle calibration log.

15.0 DATA REVIEW AND REPORTING

15.1 All samples should be updated to QC batches in the LIMS system. The analyst is responsible for reviewing all data for compliance with the QC outlined in this SOP. They are responsible for making sure that the raw data is fully documented and it is loaded into the LIMS system. They are responsible for submitting samples for redigestion and reanalysis, when appropriate.

15.2 After the analyst review is completed, the supervisor or a designated reviewer shall review the run for technical compliance to the SOP. The reviewer is also responsible for making sure that the QC calculations are done correctly and that appropriate flags are added.

15.3 After the reviewer completes their review, the data is released for client access in the LIMS. The raw data and the run log are submitted to the area manager. The manager periodically does an additional review on data for technical completeness. Any hardcopy raw data is transferred to the report generation department for scanning and storage. Instrument data is transferred electronically.

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP.

All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 16.2.

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non hazardous aqueous wastes.

16.2.2 Hazardous aqueous wastes.

16.2.3 Chlorinated organic solvents.

16.2.4 Non-chlorinated organic solvents.

16.2.5 Hazardous solid wastes.

16.2.6 Non hazardous aqueous wastes.

17.0 ADDITIONAL REFERENCES

17.1 Leeman Hydra AA instrument manual.

17.2 Leeman Hydra AA II instrument manual.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

FN: EMP070-14
Pub Date: 11/04/1996
Rev Date: 9/08/11
Page 1 of 7

Lab Manager Nancy Cole

QA Manager [signature] for Phil Worby

Effective Date: 9/12/11

TITLE: DIGESTION OF NON-POTABLE WATERS FOR ICP OR ICP-MS ANALYSIS.

REFERENCES: SW846 3010A

Revised Sections: ***8.5, 10.3.5***

1.0 SCOPE & APPLICATION

1.1 This method is applicable for the digestion of aqueous samples, TCLP extracts, and wastes that contain small amounts of suspended solids. After digestion, the samples can be analyzed by ICP or by ICP-MS. This digestion method is based on SW846 3010A.

2.0 SUMMARY

2.1 Samples for metals analysis are digested on a hot plate or in a digestion block at 90 to 95° C to solubilize the metals before analysis. Nitric and hydrochloric acids are used for digestion.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. See determinative method.

3.2 Method Detection Limit. MDLs must be established using a solution spiked at approximately 3 to 5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of three replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs must be determined approximately once per year for frequently analyzed parameters.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a batch. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample must be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results must be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and must be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs are determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over

the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. All digestions must be done in a hood. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Expose to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemical specified in this method. A reference file of date handling sheets must be made available to all personnel involved in these analyses.

6.0 COLLECTION, PRESERVATION, & HOLDING TIMES

6.1 All samples must be preserved with nitric acid at the time of collection to a pH of < 2.

6.1.1 Samples received without preservation must be preserved following the specifications in the Accutest QSM.

6.2 All samples must be digested and analyzed within 6 months of the time of collection.

7.0 APPARATUS AND MATERIALS

7.1 The apparatus needed for this digestion procedure are listed below. It should be noted that hot plates and beakers with watch glasses may be used in place of the digestion block and digestion tubes.

7.2 Digestion block. Temperature adjustable and designed to hold sample digestion tubes and capable of maintaining temperatures from 90 to 95°C.

7.3 Thermometers, calibrated with NIST traceable thermometers. To be used to monitor digestion temperatures.

7.4 Sample digestion tubes and ribbed watch glasses.

7.4.1 If sample digestion tubes are used to measure initial and final volumes, then they must be calibrated following the procedure outlined in EMP203, the digestion tube calibration SOP.

7.5 Automatic pipeter bottles.

7.6 50 ml volumetric flasks or 50 ml TD volumetric cylinders (Class A).

7.6.1 All glassware must be washed with soap and tap water and then soaked in a 10% nitric acid bath for several hours. It must then be rinsed at least 3 times with distilled, deionized water.

7.7 Glass funnels.

7.8 Whatman #41 filter paper or equivalent.

7.9 Volumetric pipets, class A.

7.10 pH paper.

8.0 STANDARDS & REAGENTS

8.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required.

8.2 Hydrochloric acid. Baker instra-analyzed or equivalent.

8.3 Nitric Acid. Baker instra-analyzed or equivalent.

8.4 Metals Spiking Solutions. All metals spiking solutions must be made up in a solution of 2 % nitric acid following the procedures outlined in the metals standards preparation SOP.

8.5 Hydrogen Peroxide, 30%. (Used only if sulfur is an analyte of interest).

9.0 INTERFERENCES

9.1 Organics in a matrix may cause interferences if the sample is not digested rigorously enough. In addition, high levels of acids in the final digestate may cause interferences in the analysis. Both of these interferences can be avoided by choosing the appropriate digestion method and by bringing the sample to an appropriate final volume. For a discussion of other interferences, refer to specific analytical methods.

10.0 PROCEDURE

10.1 Below is the procedure to be followed for the digestion of aqueous samples prior to ICP or ICP-MS analysis.

10.2 Before starting the analysis, check the initial pH of the sample with pH paper and verify that it is < 2. If it is < 2, then enter a Y in the pH check column on the metals prep logs. If the sample is not < 2, then adjust it to < 2 with nitric acid and record both the initial and final pH on the digestion log.

10.2.1 For highly basic or buffered samples, where more than a few drops of acid are required, adjust an aliquot of the sample rather than the whole amount and record the amount of acid used for the adjustment.

10.2.2 Samples for TCLP matrix or leachate spikes will be received unpreserved from the TCLP leaching area. These must be aliquoted, spiked, and preserved on receipt in the metals prep area.

10.2.3 For some clients, additional documentation of the pH adjustment is necessary. For all samples from Ohio, the pH adjustment must be noted in the case narrative or conformance summary for the samples.

10.3 Measure out 50 ml of each sample into a labeled digestion tube or into a beaker. The sample may be measured by using a graduated cylinder or by using a calibrated digestion tube. Make sure that the sample identification is accurately recorded with the digestion tube/beaker numbers on the sample digestion log. In addition to the samples, a Spike Blank or a Lab Control and a Method Blank must be set up with each batch of 20 samples or less. A Matrix Spike and a Matrix Spike Duplicate (or Matrix Duplicate) must be set up with each batch of 20 samples. Matrix Spike Duplicates are normally used unless otherwise specified by client requirements. Check with the metals supervisor for spiking levels to use for the matrix spikes and the spike blank or lab control.

10.3.1 For the method blank, add 50 ml of deionized water to the digestion tube.

10.3.2 For the lab control, add 50 ml of lab control solution to the digestion tube. Refer to the metals spiking solution SOP, EMP202, for information on the preparation of the lab control solution.

10.3.3 For the matrix spike and matrix spike duplicates, add the spiking solution directly to the 50 ml of sample in the designated tubes. Refer to the metals spiking solution SOP, EMP202, for information on the preparation and amounts of spiking solution required.

10.3.4 TCLP blank spikes must be prepared using 50 ml of the appropriate TCLPE extraction fluid.

10.3.5 If the sample is going to be analyzed for sulfur by method 6010, then add 5 ml of peroxide at room temperature to the sample and QC and let them sit for 30 minutes before proceeding. The purpose of this step is to oxidize any sulfide that is present before the digestion.

10.4 Add 1.5 ml of concentrated nitric acid to all quality control and samples.

10.5 Place the labeled tubes into a digestion block and cover with watch glasses. (If using beakers, cover the beakers with watch glasses and place them on a hot plate.) Heat the samples at 90 to 95°C until they come to a gentle reflux and then continue to heat the samples until they are evaporated to near dryness, for example 10 ml or less. After the heating is complete, allow the samples to cool.

10.5.1 Watch glasses may be removed if necessary to allow for faster volume reduction, but should be left on for the maximum time possible to limit contamination.

10.6 Add an additional 1.5 ml of concentrated nitric acid to all quality control and samples. Continue heating the samples at a gentle reflux until the sample is completely digested. (More acid may be added as necessary to complete the digestion.)

10.6.1 Signs of a complete digestion are if the digestate is light in color and/or if the appearance of the sample does not change with continued refluxing.

10.7 Add 5 ml of 1:1 HCl to each sample and reflux for an additional 15 minutes.

10.8 Wash down the beaker walls and watch glass with DI water. Bring the sample to a final volume of 50 ml with deionized water. The sample is now ready for analysis by ICP.

10.8.1 If the sample contains particulate, it can be filtered through Whatman # 41 filter paper (or equivalent) before analysis. If any samples in a batch are filtered, then all of the associated quality control must also be filtered in the same manner.

10.8.2 For ICP-MS analysis, the digestate is normally further diluted at the instrument before analysis (at least by a factor of 2) and the dilution factor must be added to the instrument file.

11.0 QUALITY ASSURANCE

11.1 A sample batch is defined as a maximum of 20 field samples in a preparation batch over a time period of 24 hours. A matrix spike/matrix spike duplicate, matrix spikes and/or duplicate is required every 20 samples.

11.2 For each digestion batch of 20 samples or less, a lab control (and a spike blank) and a method blank is prepared. Besides a lab control, a spike blank is also digested when analyzing the odd elements, such as B, Si, Sr, Sn and Pd.

11.3 For every 20 samples, digest a matrix spike/matrix spike duplicate pair instead of a matrix spike/ duplicate pair unless otherwise requested by a client.

11.4 Refer to the analytical methods SOPs for additional information on method quality control.

12.0 DOCUMENTATION

12.1 All digestion information must be entered on a digestion log. The information required includes the sample identification, the initial sample volume, the final sample volume, the initial sample pH, the acids used (including both amount and lot number), the spikes used, and the digestion times and temperatures, and the thermometer identification. Both the corrected and uncorrected temperatures must be recorded. If filtration is done, the filter type and lot must also be recorded.

12.2 The analyst must write additional information such as unusual sample characteristics in the Comments section. All spiking solution information must be entered in the metals spiking solution notebook.

13.0 DATA REVIEW & REPORTING

13.1 The prep analyst is responsible for updating the samples to SCH status in the LIMS system and for entering the prep information into the LIMS. This may be done manually or electronically. When the prep information is in the LIMS, the completed paperwork must be turned into the metals supervisor for review.

13.2 The supervisor or a metals analyst reviews the preparation information and approves the data in the LIMS system.

13.3 The original paperwork is submitted to the report generation department for filing.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

14.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards,

reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 14.2.

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non hazardous aqueous wastes.

14.2.2 Hazardous aqueous wastes.

14.2.3 Chlorinated organic solvents.

14.2.4 Non-chlorinated organic solvents.

14.2.5 Hazardous solid wastes.

14.2.6 Non-hazardous solid wastes.

15.0 ADDITIONAL REFERENCES

15.1 Refer to the ICP and ICPMS analytical SOP's, the spiking procedure SOP (EMP202), and the digestion tube calibration SOP (EMP203).

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager: _____

QA Manager: _____

Effective Date: October 7, 2009

TEST NAME: **DIGESTION OF SOILS FOR ICP AND ICP-MS ANALYSIS**

REFERENCE: SW846 3050B (Revision 2, December 1996)

***Revised Sections*, 10.2.3, 10.2.4, 12.1**

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the digestion of sediments, soils, sludges, solid wastes, and wipes. After digestion, the samples can be analyzed by ICAP or by ICP-MS (or by graphite furnace AA for antimony). This digestion method is based upon SW846 method 3050B, Revision 2, 12/96.

2.0 SUMMARY

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Then hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals, this digestate is filtered and the filter paper and residues are rinsed, first with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.2 In method 3050B, the final HCl addition is not included for ICP-MS digestates as chloride is an interference for a number of elements on ICP-MS. However, the HCl is necessary for good solubility of many elements. HCl interferences at the ICP-MS can normally be addressed with corrections at the ICP-MS. Therefore it is recommended that HCl be added for ICP-MS digestions by this method unless otherwise directed by the lab supervisor or manager.

2.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 See determinative method.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK. The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE. Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER. Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and mustd be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe

handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 Non-aqueous samples should be refrigerated at the time of receipt.

6.2 All samples should be digested and analyzed within 6 months of the time of collection.

7.0 INTERFERENCES

7.1 Sludge and soil samples can contain diverse matrix types, which may contain a variety of interferences. Spiked samples can be used to determine if these interferences are adequately treated in the digestion process. For a discussion of other interferences, refer to specific analytical methods.

8.0 APPARATUS

8.1 The apparatus needed for this digestion procedure are listed below. It should be noted that hot plates and beakers with watch glasses might be used in place of the digestion block and digestion tubes.

8.2 Digestion block. Temperature adjustable and designed to hold sample digestion tubes and capable of maintaining temperatures from 90 to 95°C.

8.3 Thermometers, calibrated with NIST traceable thermometers. To be used to monitor digestion temperatures.

8.4 Sample digestion tubes and ribbed watch glasses.

8.5 Automatic pipeter bottles.

8.6 100 ml volumetric flasks.

8.7 Glass funnels.

8.8 Whatman #41 filter paper.

8.9 Top loader balance.

8.10 Volumetric Pipets, class A.

8.11 Disposable Wood Spatulas

8.12 Ceramic Mixing Bowl.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required.

9.2 Hydrochloric acid. Baker instra-analyzed or equivalent.

9.3 Nitric Acid. Baker instra-analyzed or equivalent.

9.4 Hydrogen Peroxide, 30 %.

9.5 Metals Spiking Solutions. All metals spiking solutions should be made up in a solution of 2 % nitric acid as described in Table 1. Use volumetric glassware and pipets or autopipets. Check with the metals supervisor for additional information. Different levels of spiking solutions may be used as specified by the area supervisor.

9.5.1 The expiration date for the spiking solution is defined as the earliest date of any element or compound in that solution.

9.6 Teflon Chips

10.0 PROCEDURE

10.1 Weigh out an amount of wet sample equivalent to 1 g of dry sample into a numbered digestion tube. The sample should be weighed out using a top loader balance and the weights should be recorded to two places past the decimal. Make sure that the sample identification is accurately recorded with the digestion tube numbers on the sample digestion log.

10.1.1 Make sure that the sample has been thoroughly mixed before weighing out the representative sample. Discard rocks, sticks, etc. from the sample. (Refer to the SOP EQA042 for proper sample aliquoting procedures). All homogenization and sample handling should be done with wooden spatulas and ceramic (or other non-metal) bowls.

10.1.2 If the sample has a low percent solids, a larger sample size may be used to obtain a weight approximately equivalent to 1 g of dry sample. Check with the metals supervisor for additional direction with sampled with low percent solids or unusual matrices.

10.1.3 If the sample is a wipe, weighing is not necessary. Transfer the entire wipe into the labeled digestion tube and proceed with the digestion following steps 10.2 through 10.10. Extra wipes must be supplied by the client for the matrix spike or duplicate.

10.2 In addition to the samples, a spike blank or a lab control and a method blank must be set up with each batch of 20 samples or less. A matrix spike, a matrix spike duplicate or a duplicate should be set up with each batch of 20 samples. Matrix spike duplicates are normally used unless otherwise specified by client requirements. Refer to Table 1 for spiking levels to use for each MS and Spike Blank.

10.2.1 For the method blank and spike blank, instead of weighing out soil add approximately 1 g of Teflong chips to the digestion tube. Add the spiking solution to the blank spike after the chips are in the tube.

10.2.2 For some clients, a solid lab control is required rather than a blank spike. In that case, the solid lab control must be weighed out in the same manner as a sample.

10.2.3 For the matrix spike and matrix spike duplicate, refer to the metals spiking SOP, EMP202, for information on the preparation and amount of spiking solution require to be added to the sample in the digestion tube.

10.2.4 For the matrix spike and matrix spike duplicate, refer to the metals spiking SOP, EMP 202, for information on the preparation and amount of "odd metals spike" is to be added to the sample in the digest tube when necessary.

10.2.5 For additional details on spiking solutions and preparation, refer to the metals spiking sop, EMP202.

10.3 Add 10 ml of 1:1 nitric acid to all Quality Control and samples.

10.4 Place the numbered tubes into a digestion block and cover with watch glasses. (If using beakers, cover the beakers with watch glasses and place them on a hot plate.) Heat the samples at 90 to 95°C until they come to a gentle reflux and then continue to heat the samples for an additional 10 to 15 minutes. Do not allow the samples to boil. After the heating is complete, allow the samples to cool.

10.5 Add an additional 5ml of concentrated nitric acid to all quality control and samples. Heat the samples at a gentle reflux for an additional 30 minutes. Do not allow the volume to be reduced to below 5 ml. Cool.

10.5.1 If brown fumes are generated during this digestion, add an additional 5ml aliquot of concentrated nitric acid and heat for 30 more minutes. Repeat this process until no more brown fumes are generated.

10.6 Continue the digestion at 90 to 95ºC until the volume is reduced to 5 ml or for a period of 2 hours. Do not let the samples boil at any point during the digestion process.

10.7 Add 2 ml of water and 3 ml of 30 % hydrogen peroxide to each sample and reflux until the effervescence subsides. Cool.

10.7.1 The 30% hydrogen peroxide may be added in smaller or larger initial aliquots depending on the sample characteristics. If sample effervescence is suspected to be a problem, smaller aliquots should be used.

10.8 Continue to add 30 % hydrogen peroxide in 1ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. NOTE: Do not add more than a total of 10 ml of 30 % hydrogen peroxide. Continue the digestion at 90 to 95ºC until the volume is reduced to 5 ml or for a period of 2 hours.

10.9 Add 10 ml of concentrated HCl and reflux for an additional 15 minutes.

10.9.1 HCl may be omitted for some ICP-MS digestions for limited elements (As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, and Tl) at the discretion of the area supervisor or manager. However, in normal circumstances it should be added. Refer to section 2.2.

10.10 Filter the digestate through Whatman #41 filter paper (or equivalent) into 100 ml volumetric flasks. Make sure to rinse the digestion tubes and the filter paper well with deionized water. Dilute to volume with deionized water. The sample is now ready for analysis.

10.10.1 For ICP-MS analysis, the digestate should be further diluted at the instrument before analysis (normally at least by a factor of 2 to 5) and the dilution factor should be added to the instrument file.

11.0 QUALITY ASSURANCE

11.1 For each digestion batch of 20 samples or less, a lab control or a spike blank and a method blank should be prepared. Besides a lab control, a spike blank is also digested when analyzing the odd elements, such as B, Si, Sr, Sn and Pd.

11.1.1 Solid lab controls are required for some clients. Check with the metals supervisor for additional information.

11.2 For every 20 samples, a matrix spike, a matrix spike duplicate or a duplicate should be prepared. Matrix spike duplicates are normally used unless otherwise specified by the client requirements.

11.3 If a batch is a running batch, samples can be added to the batch (along with a method blank and spike blank or lab control) up to a maximum of 2 weeks.

11.3.1 Running batches are not allowed for all clients. Check with the metals supervisor for additional information.

11.4 Refer to the analytical methods SOPs for additional information on method quality control.

12.0 DOCUMENTATION

12.1 All digestion information should be entered on a digestion log. The information required includes the sample identification, the initial sample weight, the final sample volume, the acids used (including both amount and lot number), the spikes used, and the digestion times, temperatures, and the thermometer identification. Both the corrected and uncorrected temperature must be recorded.

12.2 The analyst should write additional information such as unusual sample characteristics in the Comments section. All spiking solution information should be entered in the metals spiking solution notebook.

12.3 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

12.4 Certificates of analysis for all primary stocks must be kept on file. If a certificate is received in the lab, give the original to the area supervisor for submission for filing with the QA department.

13.0 DATA REVIEW & REPORTING

13.1 The prep analyst is responsible for updating the samples to SCH status in the LIMS system and for entering the prep information into the LIMS. This may be done manually or electronically. When the prep information is in the LIMS, the completed paperwork should be turned into the metals supervisor for review.

13.2 The supervisor or a metals analyst reviews the preparation information and approves the data in the LIMS system.

13.3 The original paperwork is submitted to the report generation department for filing.

13.4 Supervisory (or peer) personnel will review and sign all reagent documentation a minimum of once per month.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

14.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 14.2.

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.2 Non hazardous aqueous wastes.

14.2.3 Hazardous aqueous wastes.

14.2.4 Chlorinated organic solvents.

14.2.5 Non-chlorinated organic solvents.

14.2.6 Hazardous solid wastes.

14.2.7 Non-hazardous solid wastes.

15.0 ADDITIONAL REFERENCES

15.1 Refer to the ICP and ICPMS analytical SOP's and the spiking procedure SOP (EMP202).

TABLE 1: SOIL SPIKING SOLUTION FOR 6010B (1.0 g sample)

Spiking Solution	Element	Stock Conc. in mg/l	Vol. of Stock in ml	Final Vol. of Spiking Solution in ml	Spiking Solution Conc. in mg/l	Amt of spike added in ml	Final Digestate Vol. in ml	Final Conc. at the instrument in mg/l
Mixed ICP Metals	Al	200.00	NA	NA	200.00	2.00	100.00	4.00 +
	Sb	50.00			50.00			1.00
	As	200.00			200.00			4.00
	Ba	200.00			200.00			4.00
	Be	5.00			5.00			0.10
	Cd	5.00			5.00			0.10
	Cr	20.00			20.00			0.40
	Co	50.00			50.00			1.00
	Cu	25.00			25.00			0.50
	Fe	100.00			100.00			2.00 +
	Pb	50.00			50.00			1.00
	Mn	50.00			50.00			1.00
	Ni	50.00			50.00			1.00
	Se	200.00			200.00			4.00
	Ag	5.00			5.00			0.10
	Tl	200.00			200.00			4.00
	V	50.00			50.00			1.00
	Zn	50.00			50.00			1.00
Soil Mineral Mix	Al	10000.00	50.00	200.00	2500.00	2.00	100.00	50.00 +
	Fe	10000.00	50.00	200.00	2500.00			50.00 +
	Ca	10000.00	12.50	200.00	625.00			12.50
	Mg	10000.00	12.50	200.00	625.00			12.50
	K	10000.00	12.50	200.00	625.00			12.50
	Na	10000.00	12.50	200.00	625.00			12.50
Odd Metals	B	1000.00	20.00	200.00	100.00	1.00	100.00	1.00
	Mo	1000.00	20.00	200.00	100.00			1.00
	Sn	1000.00	20.00	200.00	100.00			1.00
	Sr	1000.00	20.00	200.00	100.00			1.00
	Ti	1000.00	20.00	200.00	100.00			1.00
	Pd	1000.00	20.00	200.00	100.00			1.00
	Si	1000.00	40.00	200.00	200.00			2.00
	W	1000.00						

Accutest Laboratories
Standard Operating Procedure

Lab Manager _____

QA Manager _____

Effective Date 5/30/13

TEST NAME: METHOD 8260B, VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)

METHOD REFERENCE: SW846 8260B (Revision 2, December 1996)

Revised Sections: Table 10

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the analytical procedures, which are utilized by Accutest to acquire samples for analysis of volatile organic compounds by gas chromatographic/mass spectrometric (GC/MS) following purge and trap utilizing the internal standard technique. The compounds in Table 1 may be determined by this method. An option has been included for the analysis of 1,4-Dioxane by selected ion monitoring GC/MS (GC/SIM-SIM).

1.2 This analytical method is designed for nearly all types of samples, regardless of water content, including ground water, aqueous sludges, liquors, waste solvents, oily wastes, tars, filter cakes, sediments and soils.

1.3 The applicable concentration range of this method is compound, matrix, and instrument dependent. Volatile water-soluble compounds can be included in this analytical technique. However, for some low-molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides, quantitation limits are approximately ten times higher because of poor purging efficiency. Determination of some structural isomers (i.e. xylenes) may also be hampered by coelution.

2.0 SUMMARY OF METHOD

2.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap (Method 5030/5035). Method 5030 may be used directly on ground water samples. Method 5035 is used for low-concentration and medium-concentration soils, sediments, and wastes. Medium concentration samples are preserved and stored in methanol prior to purge-and-trap analysis.

2.2 An inert gas is bubbled through a 5 ml sample contained in a specifically designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic (GC) column.

2.3 The volatile compounds are separated by the temperature programmed GC column and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.

2.4 The peaks detected are qualitated by comparison to characteristic ions and retention times specific to the known target list of compounds.

2.5 Once identified the compound is quantitated by comparing the response of major (quantitation) ion relative to an internal standard technique with an average response factor generated from a calibration curve.

2.5 Once identified the compound is quantitated by comparing the response of major (quantitation) ion relative to an internal standard technique with an average response factor generated from a calibration curve.

2.6 Additional unknown peaks with a response > 10 % of the closest internal standard may be processed through a library search with comparison to a database of approximately 75,000 spectra. An estimated concentration is quantitated by assuming a response factor of 1.

2.7 Water soluble volatile organic and other poor purging compounds maybe analyzed using this methodology, however this method is not the method of choice for these compounds and the laboratory's ability to achieve all calibration and quality control criteria for this method cannot be guaranteed. These compounds are noted as (pp) in Table 7.

2.8 The method includes an analytical option for the analysis of 1,4-Dioxane by GC/MS-SIM. The selected ions that are characteristic of the analytes of interest are analyzed using lower concentrations of calibration standards under the same MS conditions. SIM analysis is performed upon client request and is documented in the report.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The reporting limit for this method is established at the lowest concentration standard in the calibration curve and may vary depending on matrix interferences, sample volume or weight and percent moisture. Detected concentrations below this concentration cannot be reported without qualification. See Table 10.

3.1.1 Compounds detected at concentrations between the reporting limit and MDL are quantitated and qualified as "J", estimated value. Program or project specifications may dictate that "J" qualified compounds are not to be reported.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 Experimental MDLs must be determined annually for this method.

3.2.2 Process all raw data for the replicate analysis in each MDL study. Forward the processed data to the QA group for archiving.

4.0 DEFINITIONS

BLANK - an analytical sample designed to assess specific sources of laboratory contamination. See individual types of Blanks: Method Blank, Instrument Blank, Storage Blank, Cleanup Blank and Sulfur Blank.

4-BROMOFLUOROBENZENE (BFB) - the compound chosen to establish mass spectral instrument performance for volatile (VOA) analyses.

CALIBRATION FACTOR (CF) - a measure of the gas chromatographic response of a target analyte to the mass injected. The calibration factor is analogous to the Relative Response Factor (RRF) used in the Volatile and Semivolatile fractions.

CONTINUING CALIBRATION - analytical standard run every 12 hours to verify the initial calibration of the system.

CONTINUOUS LIQUID-LIQUID EXTRACTION - used herein synonymously with the terms continuous extraction, continuous liquid extraction, and liquid extraction. This extraction technique involves boiling the extraction solvent in a flask and condensing the solvent above the aqueous sample. The condensed solvent drips through the sample, extracting the compounds of interest from the aqueous phase.

EXTRACTED ION CURRENT PROFILE (EICP) - a plot of ion abundance versus time (or scan number) for ion(s) of specified mass (Es).

INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the mass spectrometer to the target compounds.

INTERNAL STANDARDS - compounds added to every standard, blank, matrix spike, matrix spike duplicate, sample (for volatiles), and sample extract (for semivolatiles) at a known concentration, prior to analysis. Internal standards are used as the basis for quantitation of the target compounds.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is <u>not</u> synonymous with phase (liquid or solid).

MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MATRIX SPIKE DUPLICATE - a second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

METHOD BLANK - an analytical control consisting of all reagents, internal standards and surrogate standards that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background and reagent contamination.

METHOD DETECTION LIMITS (MDLs) - The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

PERCENT DIFFERENCE (%D) - As used in this SOP and elsewhere to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero. (In contrast, see relative percent difference.)

PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105°C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 ^{o}C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

PRIMARY QUANTITATION ION - a contract specified ion used to quantitate a target analyte.

REAGENT WATER - water in which an interferant is not observed at or above the minimum detection limit of the parameters of interest.

RECONSTRUCTED ION CHROMATOGRAM (RIC) - a mass spectral graphical representation of the separation achieved by a gas chromatograph: a plot of total ion current versus retention time.

RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP and elsewhere to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. (In contrast, see percent difference.)

RELATIVE RESPONSE FACTOR (RRF) - a measure of the relative mass spectral response of an analyte compared to its internal standard. Relative Response Factors are determined by analysis of standards and are used in the calculation of concentrations of analytes in samples.

RELATIVE RETENTION TIME (RRT) - the ratio of the retention time of a compound to that of a standard (such as an internal standard).

INSTRUMENT BLANK – a system evaluation sample containing lab reagent grade water with internal standards and surrogate standards added. An instrument blank is used to remove and/or evaluate residual carryover from high level standards, spike samples and field samples.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

5.3 The following analytes covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Primary standards of these toxic compounds must be prepared in a hood. A NIOSH/Mass approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

6.0 INTERFERENCES

6.1 The data from all blanks, samples, and spikes must be evaluated for interferences.

6.2 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of

the analysis by running laboratory reagent blanks. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

6.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

6.4 Contamination by carry-over can occur whenever high level and low-level samples are sequentially analyzed.

6.4.1 Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of an instrument blank to check for cross contamination. Refer to Table 11 for compounds that may cause carryover for this method.

6.4.2 It may be necessary to wash the purging device with methanol, rinse it with organic-free water, and then dry the purging device in an oven at 105^0 C. Follow the instrument manual for instructions on cleaning. Document the occurrence in the maintenance log and notify the manager/supervisor.

6.4.2.1 Clean and bake purging tube.

6.4.2.2 Clean or replace purge needle.

6.4.2.3 Clean and bake sample filter or sparge filter.

6.4.2.4 Clean and bake sample loop.

6.4.2.5 Replace trap if necessary.

6.4.2.6 Replace water management module if necessary.

6.4.2.7 Rinse transfer line with methanol. <u>Caution:</u> disconnect the trap before rinsing.

6.4.3 In extreme situations, the entire purge-and trap device may require dismantling and cleaning. Follow the instrument's manual for instructions on disassembly. Document the occurrence in the maintenance log and notify the manager/supervisor. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples.

6.4.4 If the contamination has been transferred to gas chromatograph, any of the following approaches may be used to cleanup the instrument.

6.4.4.1 Baking out the column between analyses.

6.4.4.2 Change the injector liner to reduce the potential for cross-contamination.

6.4.4.3 Remove a portion of the analytical column in the case of extreme contamination.

6.4.5 The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are stripped from the chromatographic column.

6.4 Special precautions must be taken during the analysis to avoid contamination from methylene chloride and other common laboratory solvents.

6.5.1 The sample storage and analytical area should be isolated from all atmospheric sources of methylene chloride or other common solvents.

6.5.2 Laboratory clothing worn by the analyst should be clean and used in designated areas only. Clothing previously exposed to solvent vapors in the organics sample preparation laboratory can contribute to sample contamination.

7.0 SAMPLE HANDLING AND PRESERVATION AND HOLDING TIME

7.1 HANDLING and PRESERVATION

7.1.1 Water samples

7.1.1.1 Container - 40 ml glass screw-cap VOA vial with Teflon-faced silicone septum. The 40-ml glass VOA vials are pre-cleaned and certified.

7.1.1.2 Collect all samples in duplicate. Test all samples for residual chlorine using test paper for free and total chlorine. If samples contain residual chlorine, three milligrams of sodium thiosulfate should be added for each 40 ml of water sample.

7.1.1.3 Fill sample bottles to overflowing, but do not flush out the dechlorinating agent. Sample should be taken with care so as to prevent any air or bubbles entering vials creating headspace.

7.1.1.4 Adjust the pH of all samples to ≤ 2 at the time of collection, but after dechlorination, by carefully adding two drops of 1:1 HCl for each 40 ml of sample. Seal the sample bottles, Teflon face down, and mix for one minute. Or VOA vials containing the preservative(HCL) may be used.

<u>Note</u>: Do not mix the sodium thiosulfate with the HCl in the sample bottle prior to sampling.

7.1.1.5 The samples must be protected from light and refrigerated at 0 - ≤ 6 °C from the time of receipt until analysis.

7.1.2 Soil Samples

7.1.2.1 Refer to the SOP for SW846 Method 5035 for preservation requirement of non-aqueous solids. For Ohio VAP freezing is not allowed; samples must be preserved with sodium bisulfate.

7.2 HOLDING TIME

7.2.1 Water Samples.

7.2.1.1 All samples are to be analyzed within 14 days of sampling (HCl preserved for aqueous sample) unless otherwise specified by the contract. The sample preservation deficiency is noted in the analytical run logbook when the analyst checks the pH at the bench. If the pH is not <2, the analyst notifies the supervisor, who then notifies Client Service Dept. A comment is added to the result page and Non-Conformance Summary.

7.2.2 Soil Samples

7.2.2.1 Refer to the SOP for SW846 Method 5035 for holding time requirement of non-aqueous solids.

7.2.2.2 All samples are analyzed within 14 days of sampling unless otherwise specified.

8.0 APPARATUS AND MATERIALS

8.1 SYRINGE

8.1.1 10, 25, 50, 100, 500 and 5000 µl graduated syringes, manually held (Hamilton/equiv.).

8.1.2 5 ml and 50 ml glass gas tight syringes with Luerlok end, if appropriate for the purging device.

8.2 BALANCE

8.2.1 Analytical balance capable of weighing 0.0001 gram.

8.2.2 Top loading balance capable of weighing 0.1 gram.

8.3 PURGE AND TRAP DEVICES

8.3.1 The autosampler models are used for purging, trapping and desorbing the sample into GC column.

- O.I. Model 4560 sample concentrator with 4551 vial multi-sampler
- O.I. Model 4560 sample concentrator with 4552 Water/Soil multi-sampler

8.3.2 The sample purge vial must be designed to accept 5 ml samples with a water column at least 3 cm deep.

8.3.3 The auto-sampler is equipped with a heater capable of maintaining the purge chamber at 40 °C to improve purging efficiency. The heater is to be used for low level soil/sediment analysis, but not for water or medium level soil/sediment analysis.

8.3.4 The OI #10 trap is 42 cm with an inside diameter of 0.105 inches. The trap must be packed to contain the following absorbents (3-ring) and should be conditioned at 180 °C for 30 minutes by backflushing with a Helium gas flow at least 20 ml/min before initial use.

- Tenax (2,6-Diphenylene oxide polymer).
- Silica gel.
- Carbon Molecule Sieve (CMS).

8.3.5 The desorber should be capable of rapidly heating the trap to 190^0 C for desorption. Do not exceed 210 ^{0}C during bake-out mode. Alternatively, follow manufacturer's instructions.

8.3.6 The response of chloromethane and bromonethane can be tracked for thermal decomposition products formed. If levels over the calibration requirement, the trap must be replaced and the system re-calibrated after the manager/supervisor been notified.

8.4 GAS CHROMATOGRAPH/MASS SPECTROMETER SYSTEM

8.4.1 Gas Chromatograph.

8.4.1.1 An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

8.4.1.2 The injection port should be suitable for split or splitless with appropriate interface.

8.4.1.3 The narrow bore capillary column is directly coupled to the source for HP-6890 model.

8.4.1.4 The wide bore capillary column is interfaced through a jet separator to the source for HP-5890 model.

8.4.2 Column.

- 75 m x 0.53mm ID x 3 μm film thickness capillary column coated with DB-624 (J&W Scientific), or equivalent. Condition as per manufactures directions.

- 105 m x 0.53mm ID x 3 μm film thickness capillary column coated with HP-VOA, or equivalent. Condition as per manufactures directions.

- 60 m x 0.25mm ID x 1.4 μm film thickness capillary column coated with DB-624 (J&W Scientific), or equivalent. Condition as per manufactures directions.

- 60 m x 0.45mm ID x 1.7 μm film thickness capillary column coated with DB-VRX (J&W Scientific), or equivalent. Condition as per manufactures directions.

8.4.3 Mass Spectrometer.

8.4.3.1 HP5973 or HP5970 is capable of scanning from 35 to 300 amu every 2 seconds or less, utilizing a 70 volt (nominal) electron energy in the electron impact ionization mode.

8.4.3.2 The mass spectrometer must be capable of producing a mass spectrum which meets all the criteria in Table 3 when injecting or purging 50 ng of the GC/MS tuning standard - Bromofluorobenzene (BFB).

8.4.3.3 SIM Mode – Capable of selective ion grouping at specified retention times for increased compound sensitivity (Table 2a).

8.5 DATA SYSTEM

8.5.1 Data Acquisition and Instrument Control (HP Chemstation) **-** A computer system is interfaced to the mass spectrometer, which allows the continuous acquisition and storage on a machine-readable media (disc) of all mass spectra obtained throughout the duration of the chromatographic program.

8.5.2 Data Processing (HP Enviroquant) - The software accommodates searching of GC/MS data file for target analytes which display specific fragmentation patterns. The software also allows integrating the abundance of an EICP between specified time or scan number limits. The data system includes the recent version of the EPA/NBS or NIST98 mass spectral library for qualitative searches of non-target compounds present in the chromatogram. The data system flags all data files that have been edited manually by laboratory personnel.

8.5.3 Off line Magnetic Tape Storage Device (Lagato Networker) - The magnetic tape storage device copies data for long-term, off-line storage.

9.0 REAGENTS AND STANDARDS

9.1 Solvent

9.1.1 Methanol: purge-and-trap grade quality or equivalent. Store separately, away from the other solvents.

9.2 Reagent Water

9.2.1 Reagent water is defined as water in which an interferant is not observed at the method detection limit of the parameters of interest.

9.2.2 Reagent water is generated by either passing tap water through a bed of approximately one pound of activated carbon or by using the water purification system at Accutest that is a series of deionizers and carbon cartridges.

9.3 Stock Standard Solutions

9.3.1 Commercially prepared standards used.

9.3.1.1 EPA Method 524.2 Volatiles (78 components): Absolute (or equivalent) at 200 μg/ml or 2,000 μg/ml concentration.

9.3.1.2 Custom Volatiles Mix A: Restek (or equivalent) at 2,000 μg/ml concentration.

9.3.1.3 Custom Volatiles Mix B: Restek (or equivalent) at 2,000 - 100,000 μg/ml concentration.

9.3.1.4 VOC Gas Mixture: Ultra (or equivalent) contains 200 μg/ml or 2,000 μg/ml of the following compound**s** in methanol.

- Bromomethane
- Chloroethane
- Chloromethane
- Dichlorodifluoromethane
- Trichlorofluoromethane
- Vinyl Chloride

9.3.1.5 Multiple neat compounds.

9.3.1.6 Surrogate standard mixture: Ultra (or equivalent) at a concentration of 2,500 μg/ml each surrogate compound.

- 1,2-Dichloroethane-d_4
- Dibromofluoromethane
- Toluene-d_8
- 4-Bromofluorobenzene

9.3.1.7 Internal standard mixture: Ultra (or equivalent) at a concentration of 2,000 μg/ml for all the compounds except Tert Butyl Alcohol-d_9, which is from Absolute (or equivalent) at a concentration of 50,000 μg/ml. The following five internal standards are used that exhibit similar analytical behavior to the compounds of interest.

- 1,4-Dichlorobenzene-d_4
- 1,4-Difluorobenzene
- Chlorobenzene-d_5
- Pentafluorobenzene
- Tert Butyl Alcohol-d_9

9.3.1.8 1,4-Dioxane Solution for SIMS : Ultra (or equivalent) at 100 μg/ml in methanol .

9.3.2 Unopened stock standard (ampoules) must be stored according to manufacturer's documented holding time and storage temperature recommendations (usually placed on the ampoule).

9.3.3 After opened, stock standards, internal standards, and surrogate solutions must be replaced after 6 months (one month for purgeable gases standard) or sooner if manufacture expiration date come first or comparison with quality control check samples indicates degradation.

9.3.4 Store all stock standards in vials with minimal headspace and Teflon lid liners after open, protect from light, and refrigerate to –10°C or colder or as recommended by the standard manufacturer.

9.3.5 Return the standards to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

9.4 Internal Standard and Surrogate Solution

9.4.1 Five internal standard and surrogate spiking solutions are prepared in methanol per Table 8.A.

9.4.1.1 25 µg /ml internal standard and surrogate mixture.

9.4.1.2 250 µg /ml internal standard and surrogate mixture.

9.4.1.3 100 µg/ml surrogate mixture.

9.4.1.4 25 µg /ml internal standard mixture.

9.4.1.5 250 µg /ml internal standard mixture.

9.4.2 A calibration range must be constructed for the surrogate compounds. Accordingly, appropriate amounts of surrogates are mixed with each calibration solution to define a range similar to the target compounds.

9.4.3 Each 5 ml sample, QC sample, and blank undergoing analysis should be spiked with any one of the above spiking solutions (depending upon the type of standards addition modules used), resulting in a concentration of 50 µg/l of each compound.

9.4.4 Prepare fresh internal standard and surrogate spiking solutions every six months, or sooner, if manufacturer's expiration dates come first or if the solution has degraded or evaporated.

9.5 Secondary Dilution Standards

9.5.1 Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together.

9.5.1.1 100 µg /ml V8260 mixture: prepared from 2,000 µg /ml stock solution. (see Table 8-C)

9.5.1.2 100 µg /ml V8260 custom mixture: prepared from 2,000 µg /ml stock solution. (see Table 8-C)

9.5.1.3 100 µg /ml Gas mixture: prepared from 2,000 µg /ml stock solution. (see Table 8-C)

9.5.2 Replace after one month for non-gas mixtures (one week for gas mixtures) or sooner if manufacture expiration date come first or comparison with quality control check samples indicates degradation.

9.5.3 Store all secondary dilution standards in vials with no headspace and Teflon lid liners, protect from light, and refrigerate to – 10°C or colder or according to manufacturer's storage temperature recommendation.

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9.5.4 Return the standards to the freezer as soon as preparation is finished to prevent the evaporation of volatile compounds.

9.6 Aqueous Calibration Standard Solutions

9.6.1 Initial Calibration Standards

9.6.1.1 Prepare a minimum of five aqueous calibration standard solutions containing the surrogate compounds as Table 8-D.1 or 8-D.2.

9.6.1.2 To prepare a calibration standard, add a measured volume of secondary dilution standard solutions and the surrogate spiking solution to an aliquot of reagent water in the flask. Use a micro-syringe and rapidly inject the methanol standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Bring to volume. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask.

9.6.1.2.1 1,4-Dioxane for SIMS analysis is prepared from primary stock standard (100ppm).

9.6.2 Continuing Calibration Standard

9.6.2.1 A continuing calibration standard at a concentration of 50 µg/l is prepared as the scheme outlined in Table 8-E.

9.6.3 Aqueous standards are not stable and may be stored up to 24 hours if held in Teflon sealed screw-cap vials with zero headspace at 4^{0}C (± 2^{0}C). Protect the standards from light. If not so stored, they must be discarded after use, unless they are set up to be purged by an autosampler.

9.6.4 When using an autosampler, standards may be retained up to 12 hours if they are in purge tubes connected via the autosampler to the purge and trap device.

9.7 Second Source Calibration Check Standard (ICV)

9.7.1 Prepare the second source calibration check standards from separate sources of stock standards from the calibration curve following the procedures in Section 9.6. At a minimum, an ICV should be analyzed with every initial calibration.

9.7.2 For 1,4-Dioxane via SIMS: Prepare the second source calibration check standard using 2.5 µl of a 1000ppm (Absolute or equivalent) to 50 mL of reagent water which yields a 50 ppb standard.

9.8 4-Bromofluorobenzene (BFB) Standard

9.8.1 Two BFB solutions are prepared in methanol per Table 8-B.

9.8.1.1 25 µg /ml solution for direct injection.

9.8.1.2 250 μg /ml solution for purging.

9.8.2 The solution must be replaced after 6 months or sooner if mass spectrum indicates degradation or if manufacture expiration date comes first.

10.0 CALIBRATION

10.1 Daily Maintenance. Routine Daily maintenance must be performed before any tuning, calibration or sample analysis activities are initiated. These include checks of the following items:

Purge and Trap Device:

Clean & bake purge tube
Bake trap and transfer lines
Check or refill internal/surrogate spike solution on SIM/SAM vials
Clean/replace syringe (if necessary)
Change and refill rinse bottle
Empty and rinse waste bottle

GC Oven: (if necessary)

Change septum
Change liner
Clip column, indicated by carbon build-up

10.2 Initial Calibration

10.2.1 The calibration range covered for routine analysis under RCRA, and SIM, employs standards of 1(specified compounds only), (2)*, 5, 10, 20, 50, 100, 200,(300 or 400)* μg/l. (*instrument dependent). A minimum of five standards must be run sequentially. The low calibration standard defines the reporting limit. Lower concentration standards (1.0 or 2.0 μg/l) may be needed to meet the reporting limit requirements of state specific regulatory programs. Refer to Table 8-D-1 and 8-D-2 for calibration standard preparation.

10.2.2 A calibration range must be constructed for each surrogate compound. Accordingly, add appropriate amounts of each surrogate compound to the calibration solution to define a range similar to the target compounds.

10.2.2.1 For most samples and spikes both the internal standard and the surrogate are added automatically. When doing an initial calibration surrogates are added manually. In order to compensate for the difference between the automatic and manual surrogate additions a correction factor must be applied to the amount of surrogate added in Table 8-D. To determine the correction factor divide the surrogate concentration from an automatic injection by the surrogate concentration from a manual injection for each of the surrogates. Average the result for each of the surrogates to determine the correction factor. Finally multiply the correction factor by the appropriate amount of surrogate from Table 8-D and add this amount to the standard.

10.2.3 For water and medium-level soil calibration: Transfer and fill up (no air space) each standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

10.2.4 For low-level soil calibration: Transfer 5 ml of each standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

10.2.4.1 When calibrating for Method 5035 low-level samples, if the sodium bisulfate option was used, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of each standard into vial otherwise do not add sodium bisulfate. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds. Cap the vial with Teflon septum and place it into O.I sample tray.

10.2.5 The linear range covered by this calibration is the highest concentration standard.

10.2.6 Program the autosampler to add internal standard mixture to each standard. This results in a concentration of 50 µg/l for each internal standard.

10.2.6.1 For O.I. SIM spiker: Automatically adds 10 µl of 25 µg/ml internal standard solution (Section 9.4.1.4) to each standard.

10.2.6.2 For O.I. SAM spiker: Automatically adds 1 µl of 250 µg/ml internal standard solution (Section 9.4.1.5) to each standard.

10.2.7 Analyze the standard solutions using the conditions established in Section 11.0. Whenever the highest concentration standard is analyzed, it is usually followed by the analyses of two reagent water blanks. Further analysis may not proceed until the blank analysis is demonstrated to be free of interferences.

10.2.8 Each analyte is quantitatively determined by internal standard technique using the closest eluting internal standard and the corresponding area of the major ion. See Table 7.

10.2.9 The Response Factor (RF) is defined in Section 13.1. Calculate the mean RF for each target analyte using minimum of five RF values calculated from the initial calibration curve.

10.2.10 For the initial calibration to be valid, the following criteria must be met.

10.2.10.1 Five compounds (System Performance Check Compounds, SPCCs) are checked for a minimum average response factor. The minimum mean response factors are listed in Table 6. If the initial calibration criteria for SPCCs are not achieved, perform corrective action before completing the calibration

10.2.10.2 The % RSD for each individual Calibration Check Compound (CCC) must be less than 30 %. This check is used to identify gross instrument operating problems. If the initial calibration criteria for CCCs are not achieved, perform corrective action before completing the calibration.

10.2.10.3 The percent relative standard deviation (% RSD) (see Section 13.2) of all target analytes must be less than 15 %.

10.2.10.4 If the average response factor criteria cannot be achieved, and if the problem is associated with one or more of the standards, reanalyze the

standards and recalculate the RSD. The instrument logbook should have clear documentation as to what the suspected problem was.

10.2.10.4.1 A calibration standard is allowed to be repeated only once; if the second trial fails, a new initial calibration must be performed. Notify the team leader/manager. Document this occurrence in the instrument log.

10.2.10.5 Alternately, if the average response factor criteria cannot be achieved, the calibration range can be narrowed by dropping the low or high point of the curve.

10.2.10.5.1 The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end.

10.2.10.6 If the average response factor criteria still cannot be achieved, employ an alternative calibration linearity model. Specifically, linear regression using a least squares approach may be employed.

10.2.10.6.1 If Linear regression is employed select the linear regression calibration option of the mass spectrometer data system. Do not force the regression line through the origin and do not employ 0,0 as a sixth calibration standard.

10.2.10.6.2 The correlation coefficient (r value) must be ≥0.99 for each compound to be acceptable.

10.2.10.6.3 Perform corrective action and recalibrate if the calibration criteria cannot be achieved.

10.2.10.7 The initial calibration criteria for this method applies to all additional compounds of concern specified by the client.

10.2.10.8 The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units.

10.3 Initial Calibration Verification (ICV) - Second Source Calibration Check Standard

10.3.1 The calibration is verified with a calibration check standard at 50 µg/l from an external source (Section 9.7). It must be analyzed immediately following the initial calibration.

10.3.2 The percent difference (% D) (Section 13.3) for this standard must meet the criteria of 20% for all the target compounds.

10.3.2.1 If % D is greater than 20%, reanalyze the second source check. If the criteria cannot be met upon re-injection, re-prepare the second source solution using a fresh ampoule and repeat the process.

10.3.2.2 If the %D criteria cannot be achieved after re-preparation of the second source, prepare a third source and repeat the process. Make fresh calibration standards using one of the two standard sources that matches each other and repeat the initial calibration.

10.4 Continuing Calibration Verification Standard(CCV)

10.4.1 A continuing calibration verification standard at a concentration near mid-level of the initial calibration range (50 µg/l) must be acquired every 12 hrs or at the beginning of each analytical batch.

10.4.1.1 For water and medium level soil analysis: Transfer and fill up (no air space) the calibration verification standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray. Analyze as per Section 11.7.

10.4.1.1.1 Vary the concentration of the continuing calibration verification standard on alternate verifications (i.e. every other calibration verification) using an alternative concentration standard. The standard selected must be lower than the midpoint calibration standard.

10.4.1.2 For low-level soil analysis: Transfer 5 ml of the calibration verification standard to labeled 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray. Analyze as per Section 11.7.

10.4.1.2.1 When calibrating for Method 5035 low-level samples, if the sodium bisulfate option was used add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the calibration verification standard into vial, otherwise do not use sodium bisulfate. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds. Analyze as per Section 11.7.

10.4.1.3 A continuing calibration standard is analyzed whenever the analyst suspects that the analytical system is out of calibration. If the calibration cannot be verified, corrective action is performed to bring the system into control. Analysis may not continue until the system is under control.

10.4.2 For the continuing calibration to be valid, all of the following specified criteria must be met.

10.4.2.1 The minimum RF for SPCC compound is shown on Table 6. Each SPCC compound in the calibration verification standard must meet its minimum response factor.

10.4.2.2 The percent difference (% D, see Section 13.3) for CCC must be less than 20%.

10.4.2.2.1 If the CCCs and SPCCs are not required analytes, such as the shortlist analysis for BTEX only, then all required project analytes must meet the 20 %D.

10.4.3 If the first continuing calibration verification(CCV) does not meet criteria, a second consecutive standard can be analyzed immediately. If the second CCV fails to meet criteria then corrective actions shall be performed. Such as: auto-tuning, routine system cleaning and routine system maintenance. Notify the team leader/manager.

10.4.3.1 If the second CCV trial fails, the lab must demonstrate acceptable performance after corrective action with two consecutive passing calibration verifications(CCVs) OR a new initial calibration. The Instrument Logbook and Maintenance Logbook must have clear documented notations as to what the problem was and what corrective action was implemented.

10.4.3.1.1 If the lab has not verified calibration, samples cannot be analyzed.

10.4.3.1.2 However, in the case where samples are analyzed on the system where the CCV does not meet the criteria the data must be flagged.

10.4.3.1.2.1 The data may be usable if the response for the verification exceed high(high bias) and the associated samples are non-detects.

10.4.3.1.2.2 If the criteria for the CCV is low (low bias), those sample results may be reported only if they exceed a maximum regulatory limit/decision level.

10.4.3.2 If the calibration verification is being performed using an auto sampler for night batch, two (2) vials of standard solution are placed in the device for analysis. The second standard must meet continuing calibration criteria and is used for calibration verification. The second check may be discarded only if there is a purge failure or incorrect spike concentration provided the first calibration standard meets the requirement. In this case, the first calibration standard is used as calibration verification following team leader/manager approval. Document this occurrence on instrument log.

10.4.3.2.1 Both CCVs must be evaluated. If vial 1 fails and vial 2 passes this meets the criteria of 10.4.3 of consecutive and immediate passing CCV.

10.4.3.2.2 If CCV number 2 fails, the analysis cannot continue unless it was determined that there was an isolated mechanical failure.

10.4.4 If any of the internal standard areas change by a factor of two (- 50% to + 100%) or the retention time changes by more than 30 seconds from the midpoint standard of the last initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

10.4.5.1 Reanalyze the continuing calibration standard. New initial calibration is required if reanalyzed standard continues to fail the internal standard requirements.

10.4.5.2 All samples analyzed while the system was out of control must be reanalyzed following corrective action.

10.5 Corrective Action Maintenance For Failed Tuning and Calibration Procedures

10.5.1 Inability to achieve criteria for instrument tuning or calibration may indicate the need for instrument maintenance. Maintenance may include routine system cleaning and replacement of worn expendables or the need for outside service if the scope of the repair exceeds the capability of the staff.

10.5.2 If maintenance is performed on an instrument, return to control must be demonstrated before analysis can continue. Return to control is demonstrated as follows:

10.5.2.1 Successful instrument tune using PFTBA.

10.5.2.2 Successful tune verification by the analysis of 4-bromofluorobenzene.

10.5.2.3 Successful initial calibration or continuing calibration.

11.0 PROCEDURE

11.1 Instrument conditions.

11.1.1 Recommended instrument conditions are listed in Table 2 and 2a (SIM only). Modifications of parameters specified with an asterisk are allowed as long as criteria of calibration are met. Any modification should be approved by team leader/manger.

11.1.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, use the same GC conditions for the analysis of all standards, blanks, samples, and QC samples.

11.2 Purge and Trap Device conditions.

11.2.1 See Table 2.

11.2.2 Daily Maintenance. Routine Daily maintenance must be performed before any tuning, calibration or sample analysis activities are initiated. These include checks of the following items:

<u>Purge and Trap Device:</u>

- Clean & bake purge tube.
- Bake trap and transfer lines.
- Check or refill internal/surrogate spike solution on SIM/SAM vials.
- Clean/replace syringe (if necessary).
- Change and refill rinse bottle.
- Empty and rinse waste bottle.

11.3 Step 1: Daily GC/MS performance check.

11.3.1 Every 12 hours, either

- Inject 2 µl (50 ng) of BFB solution directly on column or
- Purge 10 µg/l of 5ml (50ng) to GC column.

11.3.2 The GC/MS system must be checked to verify acceptable performance criteria are achieved (see Table 3).

11.3.3 This performance test must be passed before any samples, blanks or standards are analyzed. Evaluate the tune spectrum using three mass scans from the chromatographic peak and a subtraction of instrument background.

11.3.3.1 Select the scans at the peak apex and one to each side of the apex.

11.3.3.2 Calculate an average of the mass abundances from the three scans.

11.3.3.3 Background subtraction is required. Select a single scan in the chromatogram that is absent of any interfering compound peaks and no more than 20 scans prior to the elution of BFB. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the tuning compound peak.

11.3.4 If all the criteria are not achieved, the analyst must retune the mass spectrometer with team leader/manager and repeat the test until all criteria are met.

11.3.4.5 Alternatively, an additional scan on each side of the peak apex may be selected and included in the averaging of the mass scans. This will provide a mass spectrum of five averaged scans centered on the peak apex. NOTE: The selection of additional mass scans for tuning may only be performed with supervisory approval on a case by case basis.

11.3.5 The injection time of the acceptable tune analysis is considered the start of the 12-hour clock.

11.3.6 Until performance check is acceptable, then calibration check (step 2) can be analyzed.

11.4 Step 2 : Daily calibration check

11.4.1 Initial calibration

11.4.1.1 Refer to Section 10.2.

11.4.1.2 An initial calibration must be established (or reestablished) on each instrument:

- Prior to any sample analyses;
- Whenever a new column is installed;
- Whenever instrument adjustments that affect sensitivity are made; and
- Whenever a continuing calibration standard fails to meet the specified acceptance criteria, on the second trial.

11.4.2 Initial Calibration Verification - Second Source Calibration Check Standard

11.4.2.1 This standard is only analyzed when initial calibration provided. Refer to Section 10.3.

11.4.3 Continuing Calibration verification standard

11.4.3.1 Refer to Section 10.4.

11.4.4 The method blank (step 3) cannot be analyzed until the continuing calibration verification meets the criteria.

11.5 Step 3 : Method blank

11.5.1 The acceptable method blank must be analyzed for every 12-hour time period or sooner.

11.5.1.1 Water and medium-level soil samples - Place a 40 ml vial, filled with DI water onto the autosampler.

11.5.1.2 Low-level soil samples without sodium bisulfate - Transfer 5 ml of DI water to a 40 ml vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.5.1.2.1 Low-level soil samples with sodium bisulfate (Method 5035) - Add 1g of sodium bisulfate to a 40 ml vial before aliquot 5 ml of DI water into the vial and cap with Teflon septum, then place the vial onto the autosampler.

11.5.2 Program the autosampler to add internal standard and surrogate solution to the method blank for a concentration of 50 µg/l for each internal standard and surrogate.

11.5.2.1 For O.I. SIM spiker: Automatically adds 10 µl of 25 µg/ml internal standard and surrogate solution (Section 9.4.1.1) to the method blank.

11.5.2.2 For O.I. SAM spiker: Automatically adds 1 µl of 250 µg/ml internal standard and surrogate solution (Section 9.4.1.2) to the method blank.

11.5.3 No compound can be present above the laboratory's MDL. If common laboratory solvents (i.e. methylene chloride, acetone) are present in the sample between the MDL and RL, the analyst must determine if the contamination will negatively impact data quality. If the contamination impacts data quality, all affected samples must be re-analyzed.

11.5.4 Surrogates must meet recovery criteria specified in house limits.

11.5.5 If the method blank does not meet surrogate criteria or contains target analytes above the MDL, then

11.5.5.1 All samples analyzed following an out of control method blank must be reanalyzed.

11.5.5.2 Check for the potential of contamination interference from the following areas. Make sure all items are free contamination.

- the analytical system,
- dust and vapor in the air,
- glassware and
- Reagents.

11.5.5.3 Re-analyze the method blank following the system evaluation. In this situation, the instrument logbook should have clear documented notations as to what the problem was and what corrective action was implemented to enable the second blank to pass.

11.5.5.4 If re-analyzed method blank remains out of control, notify team leader or manager.

11.5.6 If two consecutive method blanks are analyzed during unattended operations, the second analysis must meet criteria for the subsequent sample analysis to be valid. Always report the second method blank. The second analysis can only be discarded because of a purge failure provided that the first blank meets the requirement. In this case, the first blank is reported following team leader/manager approval. Document this occurrence on the instrument log.

11.5.7 The blank spike (BS) (step 4) cannot be analyzed until the method blank meets criteria.

11.6 Step 4: Blank spike (BS)

11.6.1 An acceptable blank spike must be analyzed with every analytical batch. The maximum number of samples per analytical batch is twenty.

11.6.2 Spike 50 ml of reagent water with appropriate amount of the standards to prepare a blank spike containing 50 µg/L of each analyte. In situations where lower detection limits are required, a blank spike at 20 µg/L may be prepared. The stock solution for the BS must be from a different source than the initial calibration solution. Refer to Table 8-F for the preparations of the blank spikes.

11.6.2.1 Water and medium-level soil samples - Place a 40 ml vial, filled with DI water onto the autosampler.

11.6.2.2 Low-level soil samples without sodium bisulfate - Aliquot 5 ml of the blank spike into vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.6.2.2.1 Low-level soil samples with sodium bisulfate for Method 5035 - Add 1g of sodium bisulfate to labeled 40 ml vial before aliquot 5 ml of the blank spike into vial and cap with Teflon septum, then place the vial into O.I. sample tray.

11.6.3 Initiate auto addition of internal standard and surrogate into the syringe per 11.5.2.

11.6.4 Compare the percent recoveries (% R) (see Section 13.5) to the in house limits acceptance criteria. If a blank spike is out of control, all the associated samples must be reanalyzed. The exception is if the blank spike recovery is high and no hits reported in associated samples and QC batch. In that case, the sample results can be reported with footnote (remark) and no further action is required. Or if the blank spike recovery is low and the hits in the samples are above regulatory levels.

11.6.5 Do not analyze samples and MS/MSD (step 5) unless the BS meets acceptance criteria.

11.7 Step 5: Samples /MS/MSD analysis

11.7.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

11.7.2 Select the sample dilution factor to assure the highest concentration analyte is above the calibration range midpoint, but below the upper limit of the range depend on project requirements. See Table 9 for dilution guideline.

- Utilize FID screen data.
- Utilize acquired sample data.
- Utilize the history program.
- Sample characteristics (appearance, odor).

11.7.3 Water samples.

11.7.3.1 Using O.I.Model 4560 sample concentrator with 4551 or 4552 vial multisampler,

- Place the 40 ml vial in the tray, or
- Load 5ml sample into purge tube if sample volume limited.

11.7.4 Sediment/ soil sample

11.7.4.1 Low-level soil method

11.7.4.1.1 Collect the sample using the procedures detailed in the SOP for SW846 Method 5035 low - level soil samples.

11.7.4.1.2 Weigh out 5 g of each sample into a labeled vial. Add 5 ml of reagent water and cap the vial quickly. Transfer the 40ml vial to the autosampler tray. Stir and heat the sample at the time of analysis.

11.7.4.2 Medium-level soil method

11.7.4.2.1 Collect the sample using the procedures detailed in the SOP for SW846 Method 5035 medium - level soil samples.

11.7.4.2.2 Select a methanol aliquot of appropriate volume (see Table 9) determined via screening and transfer to 40 ml of reagent water.

11.7.5 Program the autosampler to inject the internal standard and surrogate solution into the robotic syringe used to withdraw sample from the 40 ml vial. This addition to 5 ml of sample is equivalent to a concentration of 50 µg/L of each internal standard and surrogate.

11.7.5.1 For O.I. SIM spiker: Automatically adds 10 µl of 25 µg/ml internal standard and surrogate solution (Section 9.4.1.1) to each sample.

11.7.5.2 For O.I. SAM spiker: Automatically adds 1 µl of 250 µg/ml internal standard and surrogate solution (Section 9.4.1.2) to each sample.

11.7.6 Purge the sample for 11 minutes with Helium.

11.7.6.1 Low-level soil sample must be performed at 40 °C while the sample is being agitated with the magnetic stirring bar or other mechanical means.

11.7.6.2 To improve the purging efficiency of water-soluble compounds, aqueous samples may also be purged at 40 °C as long as all calibration standards, samples and QC samples are purged at the same temperature and acceptable method performance is demonstrated.

11.7.7 One sample is randomly selected from each analytical batch of similar matrix types and spiked in duplicate to determine whether the sample matrix contributes bias to the analytical results. A matrix spike and matrix spike duplicate are performed by spiking the sample for a concentration of 50 µg/l or 50 µg/kg based on 5 g dry weight. In situations where lower detection limits are required, a blank spike at lower concentration may be prepared.

11.7.8 Desorb the sample for 4 minutes by rapidly heating the trap to 190 °C while backflushing with Helium. Desorb time may require performance optimum between 2.0 and 4.0 minutes as dictated by trap manufacturers specifications or instrument characteristics.

11.7.9 Program the purge and trap system to automatically rinse purge tube at least twice with heated organic-free water (reagent water) between analyses to avoid carryover of target compounds. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with methanol solution between analyses, rinse it with distilled water.

11.7.10 Bake the trap at least 10 minutes at 210 °C to remove any residual purgeable compounds.

11.7.11 If the initial analysis of the sample or a dilution of the sample has a response for any ion of interest that exceeds the working range of the GC/MS system, the sample must be reanalyzed at a higher dilution.

11.7.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

11.8 Sample dilutions

11.8.1 Using Screening Data to Determine Dilution Factors

11.8.1.1 Dilution for High Concentration Analytes Exceeding The Calibration Range

11.8.1.1.1 The highest concentration target compound detected in the screen data is compared to the highest concentration calibration standard used for determinative volatile organics analysis.

11.8.1.1.1.1 Divide the calibration concentration of the highest concentration calibration standard by the screen concentration.

11.8.1.1.1.2 If the result is >1, sample dilution is considered.

11.8.1.1.2 The result from step 11.8.1.1.1 determines the dilution factor. The dilution factor is targeted to assure that the highest concentration diluted analyte is at the mid-range concentration of the calibration curve for the determinative analysis.

11.8.1.1.3 In all cases a conservative approach to dilution is applied to minimize the increase of detection and reporting limits

11.8.1.2 Dilution for High Concentration Matrix Interferences

11.8.1.2.1 The peak height of the background is compared to the peak height of the later eluting calibration standards from the screening analysis.

11.8.1.2.1.1 A rough estimate of background concentration is calculated by dividing the background peak height by the peak height of the selected screening standard and multiplying by its concentration.

11.8.1.2.2 If the result is >1, sample dilution is considered.

11.8.1.2.3 The result from step 11.8.1.2.1 determines the dilution factor. The dilution factor is targeted to avoid Carry-over contamination between samples and facilitate qualitative and quantitative analysis of target compounds present in the sample.

11.8.1.2.4 In all cases a conservative approach to dilution is applied to minimize the increase of detection and reporting limits

11.8.2 If the concentration of any target compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and re-analyzed. Until the diluted sample is in a sealed sample vial, all steps in the dilution procedure must be performed without delay.

11.8.3 Water Samples.

11.8.3.1 Prepare all dilutions of water samples in volumetric flasks (10 ml to 100 ml). Intermediate dilutions may be necessary for extremely large dilutions.

11.8.3.2 Calculate the approximate volume of reagent water, which will be added to the volumetric flask, and add slightly less than this quantity to the flask. Refer to Table 9 for dilution guideline.

11.8.3.3 Inject the proper sample aliquot from a syringe into the volumetric flask. Dilute the flask to the volume mark with reagent water. Cap the flask and invert the flask three times.

11.8.3.4 Fill a 40 ml sample vial and seal with a Teflon baked silicon septa, load the diluted sample into the autosampler and analyze according to Section 11.7.

11.8.3 Low-level Soil Samples.

11.8.3.1 The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low-level soil method or the medium-level soil method.

11.8.3.2 If any target compound exceeds the initial calibration range from the analysis of 5 g sample, a smaller sample size must be analyzed. However, the smallest sample size permitted is 0.5 g. If smaller than 0.5 g sample size is needed to prevent any target compounds from exceeding the initial calibration range, the medium level method must be used.

11.9 Data interpretation

11.9.1 Qualitative identification.

11.9.1.1 The targeted compounds shall be identified by analyst with competent knowledge in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound.

11.9.1.2 The characteristic ions for target compounds that can be determined are listed in Table 7. Table 4 and Table 5 list the characteristic ions for internal standards and surrogate compounds respectively.

11.9.1.3 The criteria required for a positive identification are listed below.

11.9.1.3.1 The sample component must elute at the same relative retention time (RRT) as the daily standard. Criteria are the RRT of sample component must be within ± 0.06 RRT units of the standard component.

11.9.1.3.2 The relative intensities of these ions must agree within ± 30 % between the daily standard and sample spectra. (Example: For an ion with an abundance of 50 % in the standard spectra, the corresponding sample abundance must be between 20 and 80 %.)

11.9.1.3.2.1 Compounds can have secondary ions outside criteria from co-eluting compounds and/or matrix effect that can contribute to ion abundances. The interference on ion ratios can't always be subtracted out by software programs resulting in qualified compound identification.

11.9.1.3.2.2 Quantitation reports display compounds that have secondary ions outside the ratio criteria with a "#" flag.

11.9.1.3.2.3 Any quant reports with compounds that are deemed to be reportable despite the "#" flag, will be initialed in the "#" column by the analyst. Further review to the reporting of qualified compounds will be done by a supervisor or team leader and initialed on the quantitation.

11.9.1.3.3 Structural isomers that produce very similar mass specrtra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25 % of sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

11.9.2 Quantitative analysis

11.9.2.1 Once a target compound has been identified, its concentration (Section 13.4) will be based on the integrated area of the quantitation ion, normally the base peak (Table 7). The compound is quantitated by internal standard technique with an average response factor generated from the initial calibration curve.

11.9.2.2 If the sample produces interference for the primary ion, use a secondary ion to quantitate (see Table 7). This is characterized by an excessive background signal of the same ion, which distorts the peak shape beyond a definitive integration. Also interference could severely inhibit the response of the internal standard ion. This secondary ion must also be used to generate new calibration response factors.

11.10 Library search for tentatively identified compounds.

11.10.1 If a library search is requested, the analyst should perform a forward library search of NBS or NIST98 mass spectral library to tentatively identify 15 non-reported compounds.

11.10.2 Guidelines for making tentative identification are listed below.

11.10.2.1 These compounds should have a response greater than 10 % of the nearest internal standard. The response is obtained from the integration for peak area of the Total Ion Chromatogram (TIC).

11.10.2.2 The search is to include a spectral printout of the 3 best library matches for a particular substance. The results are to be interpreted by analyst.

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

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

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

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

11.10.2.7 Ions present in the reference spectrum but not in the sample spectrum should be verified by performing further manual background subtraction to eliminate the interference created by coeluting peaks and/or matrix interference.

11.10.2.8 Quantitation of the tentatively identified compounds is obtained from the total ion chromatogram based on a response factor of 1 and is to be tabulated on the library search summary data sheet.

11.10.2.9 The resulting concentration should be reported indicating: (1) that the value is estimate, and (2) which internal standard was used to determine concentration. Quantitation is performed on the nearest internal standard.

11.11 An instrument blank is a system evaluation sample containing lab reagent grade water with internal standards and surrogates. An instrument blank is used to remove and or evaluate residual carryover from high level standards, spike samples and field samples. Since target compound lists have expanded to overlap some volatile and semi-volatile compounds, instrument blanks are necessary to remove carryover contamination.

11.11.1 The compounds that may exhibit carryover for this method are listed in Table 11.

11.11.2 If instrument blanks following a standard or spike sample exhibits carrry-over effect, then any samples that show the same carryover profile, after a comparable concentration must be considered suspect and rerun for confirmation. For example, if an instrument blank has 1ppb detected after a 200ppb standard, then any sample following a sample containing 200ppb or above of the same compound must be confirmed for possible carryover.

11.11.3 If an Instrument Blank(s) was run following suspect high concentration samples and it exhibits the same carryover profile after a comparable concentration must be considered suspect and rerun for confirmation.

11.11.4 In some cases, several instrument blanks may have to be run to eliminate contamination from over loaded samples.

11.11.5 The analytical system is considered free of carryover, when no target analytes can be detected above the MDL.

11.12 Selected Ion Monitoring (SIM) Option Selected Ion Monitoring (SIM) Option

11.12.1 Instrument Set-Up: Modify the method for SIM analysis and define ion groups with retention times, ions and dwell times to include base peak ion for the target compounds of interest, surrogates, and internal standards (Table 2a.) Select a mass dwell time of 50 milliseconds for all compounds.

11.12.2 Calibration: Calibrate the mass spectrometer in the selected ion monitoring mode using 6 calibration standards of 5, 10, 20, 50, 100, 200 ug/l. Spike each standard with the SIM specific internal standard solution at 4ug/ml. Calculate individual response factors and response factor RSDs.

11.12.3 Initial Calibration Verification. Verify the initial calibration after its completion using a 50 ug/l calibration standard purchased or prepared from a second standards reference materials source. The initial calibration verification must meet the criteria of Section 10.2.

11.12.4 Continuing Calibration Verification. Verify the initial calibration every 12 hours using a 50 ug/l calibration. The continuing calibration verification must meet the criteria of Section 10.4.

11.12.5 Surrogate Standard Calculation.. Report surrogate spike accuracy for the surrogates spiked for the full scan GC/MS analysis.

12.0 QUALITY CONTROL

12.1 QC Requirements Summary

BFB	Beginning of the analytical shift and every 12 hours
ICV - Second Source Calibration Check Standard	Following initial calibration
Calibration Verification Standard	Every 12 hours
Method Blank	Every 12 hours
Blank Spike	One per analytical batch*
Matrix Spike	One per analytical batch*
Matrix Spike Duplicate	One per analytical batch*
Surrogate	Every sample and standard
Internal Standard	Every sample and standard

*The maximum number of samples per analytical batch is twenty.

12.2 Daily GC/MS Performance Check - BFB

12.2.1 Refer to Section 11.3.

12.3 Second Source Calibration Check Standard

12.3.1 Refer to Section 10.3.

12.3.2 Calibration Verification Standard

12.3.3 Refer to Section 10.4.

12.5 Method Blank

12.5.1 Refer to Section 11.5.

12.6 Blank Spike

12.6.1 Refer to Section 11.6.

12.7 Matrix Spike (MS)/Matrix Spike Duplicate (MSD)

12.7.1 One sample is selected at random from each analytical batch of similar matrix types and spiked in duplicate to check precision and accuracy.

12.7.2 Assess the matrix spike recoveries (Section 13.5) and relative percent difference (RPD) (Section 13.6) against the control limits..

12.7.3 If the matrix spike recoveries do not meet the criteria, check the blank spike recovery to verify that the method is in control. If the blank spike did not meet criteria, the method is out of control for the parameter in question and should be reanalyzed or qualified with an estimate of potential bias. Otherwise, matrix interference is assumed and the data is reportable. No further corrective action is required.

12.8 Surrogates

12.8.1 All standards, blanks, samples, and matrix spikes contain surrogate compounds, which are used to monitor method performance. If the recovery of any surrogate compound does not meet the control limits, the result must be flagged and:

12.8.1.1 The calculation must be checked.

12.8.1.2 The sample must be reanalyzed if the recovery of any one surrogate is out of control limit.

12.8.2 If the sample exhibits matrix interference, defined as excessive signal levels from target or non-target interfering peaks. In this case, reanalysis may not be required following team leader/manager approval.

12.8.3 If surrogate recoveries are acceptable upon reanalysis, the data from the reanalysis is reported. If the reanalysis date did not meet the hold time, then both sets of data must be submitted with the reanalysis reported.

12.8.4 If surrogates are still outside control limits upon reanalysis, then both sets of data should be submitted with the first analysis reported.

12.9 Internal Standard

12.9.1 Retention time for all internal standards must be within ± 30 seconds of the corresponding internal standard in the latest continuing calibration or 50 µg/l standard of initial calibration.

12.9.2 The area (Extracted Ion Current Profile) of the internal standard in all analyses must be within 50 to 200 % of the corresponding area in the latest calibration standard (12 hr. time period).

12.9.3 If area of internal standard does not meet control limits, the calculations must be checked. If a problem is not discovered, the sample must be reanalyzed.

12.9.4 If areas are acceptable upon reanalysis, the reanalysis data is reported.

12.9.5 If areas are unacceptable upon reanalysis, then both sets of data are submitted with the original analysis reported.

13.0 CALCULATION

13.1 Response Factor (RF)

$$RF = \frac{As \times Cis}{Ais \times Cs}$$

where:
As = Area of the characteristic ion for the compound being measured.
Ais = Area of the characteristic ion for the specific internal standard.
Cs = Concentration of the compound being measured (ug/l).
Cis = Concentration of the specific internal standard (ug/l).

13.2 Percent Relative Standard Deviation (% RSD)

$$\%RSD = \frac{SD}{RFav} \times 100$$

where:
SD = Standard Deviation
RFav = Average response factor from initial calibration.

13.3 Percent Difference (%D)

$$\%D = \frac{(RFav - RFcv)}{RFav} \times 100$$

where:
RFcv = Response factor from Calibration Verification standard.
RFav = Average response factor from initial calibration.

13.4 Concentration (Conc.)

<u>For water:</u>

$$Conc.\ (\mu g/l) = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Vi}$$

<u>For soil/sediment low level</u> (on a dry weight basis):

$$Conc.\ (\mu g/kg) = \frac{Ac \times Cis \times Vp}{Ais \times RF \times Ws \times M}$$

<u>For soil/ sediment medium level (on a dry weight basis)</u>

$$Conc.\ (\mu g/kg) = \frac{Ac \times Cis \times Vp \times Vt}{Ais \times RF \times Vme \times Ws \times M}$$

Where:
Ac = Area of characteristic ion for compound being measured.
Ais = Area of characteristic ion for internal standard.
Cis = Concentration of internal standard
RF = Response factor of compound being measured(from initial calibration)
Vi = Initial volume of water purged (ml)
Vp = 5 ml (Total Purge Volume)
Vme = Volume of Methanol aliquot
Vt = Ml Solvent + ((100-% solid)/100 x Ws)
Ws = Weight of sample extracted (g).
M = (100 - % moisture in sample) / 100 or % solids / 100

13.5 Percent Recovery (% R)

$$\% R = \frac{\text{Concentration found}}{\text{Concentration spiked}} \times 100$$

13.6 Relative Percent Difference (RPD)

$$RPD = \frac{|MSC - MSDC|}{(1/2)(MSC+MSDC)} \times 100$$

Where:
MSC = Matrix Spike Concentration
MSDC = Matrix Spike Duplicate Concentration

13.7 Linear regression by the internal standard technique.

$$C_s = \left(\frac{\frac{A_s}{A_{is}} - b}{A} \right) \times C_{is}$$

Where:
Cs = concentration of target analyte
As = Area of target analyte
Cis = concentration of the internal standard
b = Intercept
a = slope of the line

$$a = \frac{N \Sigma xy - \Sigma x \Sigma y}{N \Sigma x^2 - (\Sigma x)^2}$$

$$b = \frac{\Sigma y - a \Sigma x}{N}$$

N = number of points
x = amount of analyte
y = response of instrument

13.8 Correlation Coefficient

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

14.0 DOCUMENTATION

14.1 The Analytical Logbook records the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

14.1.1 If samples require reanalysis, a brief explanation of the reason must be documented in the Comments section.

14.2 Standards Preparation Logbook must be completed for all standard preparations. All information must be completed; the page must be signed and dated by the appropriate person.

14.2.1 The Accutest lot number must be cross-referenced on the standard vial.

14.3 Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument. Each instrument has a separate log.

14.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

14.5 Supervisory (or peer) personnel must routinely review (at least once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

Table 1. TARGET COMPOUNDS		
Acetone	1,4-Dichlorobenzene	Methylene Bromide
Acetonitrile	Dichlorodifluoromethane	Methylene Chloride
Acrolein	1,1-Dichloroethane	1-Methylnaphthalene (1)
Acrylonitrile	1,2-Dichloroethane	2-Methylnaphthalene (1)
Allyl Chloride	1,1-Dichloroethene	Naphthalene
Benzene	cis-1,2-Dichloroethene	2-Nitropropane (1)
Benzyl chloride	trans-1,2-Dichloroethene	Pentachloroethane
Bromobenzene	1,2-Dichloropropane	Propionitrile
Bromochloromethane	1,3-Dichloropropane	Propyl Acetate (1)
Bromodichloromethane	2,2-Dichloropropane	n-Propylbenzene
Bromoform	1,1-Dichloropropene	Styrene
Bromomethane	cis-1,3-Dichloropropene	Tert Butyl Alcohol
2-Butanone (MEK)	trans-1,3-Dichloropropene	tert-Amyl Methyl Ether
Butyl Acetate (1)	1,4-Dioxane	tert-Butyl Ethyl Ether
n-Butyl Alcohol (1)	Epichlorohydrin (1)	1,1,1,2-Tetrachloroethane
n-Butylbenzene	Ethyl Acetate	1,1,2,2-Tetrachloroethane
sec-Butylbenzene	Ethyl Ether	Tetrachloroethene
tert-Butylbenzene	Ethyl Methacrylate	Tetrahydrofuran
Carbon Disulfide	Ethylbenzene	Toluene
Carbon Tetrachloride	p-Ethyltoluene (1)	trans-1,4-Dichloro-2-Butene
Chlorobenzene	Freon 113	1,2,3-Trichlorobenzene
Chlorodifluoromethane (1)	Heptane (1)	1,2,4-Trichlorobenzene
Chloroethane	Hexachlorobutadine	1,1,1-Trichloroethane
2-Chloroethyl Vinyl Ether	Hexachloroethane	1,1,2-Trichloroethane
Chloroform	Hexane (1)	Trichloroethene
Chloromethane	2-Hexanone	Trichlorofluoromethane
Chloroprene (2-chloro-1,3-butadiene)	Iodomethane (Methy iodide)	1,2,3-Trichloropropane
o-Chlorotoluene	IsoAmyl Alcohol (1)	1,2,4-Trimethylbenzene
p-Chlorotoluene	Isobutyl Alcohol	1,3,5-Trimethylbenzene
Cyclohexane (1)	Isopropyl Acetate (1)	2,2,4 Trimethylpentane
Cyclohexanone	Isopropylbenzene	Vinyl Acetate
di-Isobutylene (1)	p-Isopropyltoluene	Vinyl Chloride
di-Isopropyl Ether	Methacrylonitrile	Vinyltoluene (1)
1,2-Dibromo-3-Chloropropane	Methyl Acetate (1)	m,p-Xylene
Dibromochloromethane	3 Methyl-1-Butanol (1)	o-Xylene
1,2-Dibromoethane	Methyl Tert Butyl Ether	Ethanol
Dibromomethane (1)	Methylcyclohexane	Methyl Acrylate
1,2-Dichlorobenzene	Methyl Methacrylate	1-chloro-1,1-difluoroethane
1,3-Dichlorobenzene	4-Methyl-2-pentanone (MIBK)	1,1,1-trifluoroethane
1,1-dichloro-1-fluroethane	2,2-Dichloropropane	

(1) NELAC Accreditation is not offered for this compound. Results may not be useable for regulatory purposes in States where this accreditation option is not offered.

Table 2. RECOMMENDED OPERATING CONDITION	
Gas Chromatograph/ Mass Spectrometer	
Carrier Gas (linear velocity)	Helium at *30 cm/sec
Mass range	35 – 300 amu
Electron Energy	70 volts (nominal)
Scan time	not to exceed 2 sec. per scan
Injection port temperature	200 - 225 °C
Source temperature	200 - 250 °C
Transfer line temperature	220 - 280 °C
Analyzer temperature	220 - 250 °C
Gas Chromatograph temperature program*	
Initial temperature	*40 °C
Time 1	*3 minutes
Column temperature rate	*8 degrees/min.
Final temperature	*220 °C.- 240 °C
Total run time	*25 – 50 mins
Purge and Trap Device	
Purge time	9 min. (at 40 °C for low-level soil) SIM – 6 min @ 50 °C
Desorb**	4 min. at 190 °C
Bake	>10 min. at 210 °C
Transfer line	100 - 130 °C
Valve temperature	approx. transfer line temperature

* Parameter modification allowed for performance optimization provided operational and QC criteria is achieved.(must be approved by team leader/manager)

** Desorb time may require performance optimum between 2.0 and 4.0 minutes as dictated by trap manufacturers specifications or instrument characteristics

Table 2a – SIM Group Parameters		
Group No.	**Retention Time (minutes)**	**Ions**
1	0 – 10.8	58, 65, 66, 88
2	10.8 – 16.0	95, 174, 176, 98, 100, 70

Table 3. BFB KEY IONS AND ION ABUNDANCE CRITERIA	
Mass	**Ion Abundance Criteria**
50	15-40% of mass 95
75	30-60% of mass 95
95	Base peak, 100% relative abundance
96	5-9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5-9% of mass 174
176	>95% and <101% of mass 174
177	5-9% of mass 176

Table 4. INTERNAL STANDARD QUANTITION IONS	
Internal Standard	**Primary/Secondary Ions**
1,4-Difluorobenzene	114 / 63,88
Chlorobenzene-d5	117 / 82, 119
Pentafluorobenzene	168
1,4-Dichlorobenzene-d4	152 / 115, 150
Tert Butyl Alcohol-d9	65/66
Internal Standard (SIM)	
Tert Butyl Alcohol-d9	65/66

Table 5. SURROGATE QUANTITION IONS	
Surrogate Compound	**Primary/Secondary Ions**
1,2 Dichloroethane – d_4	102
Dibromofluoromethane	113
Toluene-d8	98
4-Bromofluorobenzene	95 / 174, 176

Table 6. CRITERIA FOR CCC AND SPCC		
Initial Calibration	Maximum % RSD for CCC is 30 %	
Continuing Calibration	Maximum % D for CCC is 20 %	
Calibration check compounds (CCC)	**Volatile Compound**	
	Vinyl chloride 1,1-Dichloroethene Chloroform 1,2-Dichloropropane Toluene Ethylbenzene	
System Performance Check Compounds (SPCC)	**Compound Name**	**Minimum RF**
	Chloromethane	0.1
	1,1-Dichloroethane	0.1
	Bromoform	0.1
	1,1,2,2-Tetrachloroethane	0.3
	Chlorobenzene	0.3

Table 7. Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)	Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Tert Butyl Alcohol-d9			Dibromomethane	93	95, 174
Tert Butyl alcohol	59	57	Di-isobutylene	57	
Ethanol	45	46	Epichlorohydrin (pp)	57	57, 49, 62, 51
Pentafluorobenzene			Ethyl methacrylate	69	69, 41, 99, 86, 114
1,1,1-Trichloroethane	97	99, 61	Heptane	57	
1,1-Dichlorethane	63	65, 83	Hexane	56	
1,1-Dichloroethene	96	61, 63	Isopropyl acetate	43	
2,2-Dichloropropane	77	97	Methyl cyclohexane	83	
2-Butanone (pp)	72	43, 72	Methyl methacrylate	69	69, 41, 100, 39
Acetone (pp)	58	43	n-Butanol (pp)	56	41
Acetonitrile (pp)	41	41, 40, 39	Propyl Acetate	43	
Acrolein (pp)	56	55,58	tert Amyl Methyl Ether	73	
Acrylonitrile (pp)	53	52, 51	Toluene	92	91
Allyl Chloride	41		Toluene-d_8	98	
Bromochloromethane	128	49, 130	trans-1,3-Dichloropropene	75	77, 39
Bromomethane	94	96	Trichloroethene	95	97, 130, 132
Carbon disulfide	76	78			
Chlorodifluouromethane	51	86	**Chlorobenzene-d5**	117	82,119
Chloroethane	64	66	1,1,1,2-Tetrachloroethane	131	133, 119
Chloroform	83	85	1,2-Dibromoethane	107	109, 188
Chloromethane	50	52	1,3-Dichloropropane	76	78
Chloroprene	53	53, 88, 90, 51	Bromoform	173	175, 254
cis-1,2-Dichloroethene	96	61, 98	Butyl Acetate	56	
Cyclohexane	84		Chlorobenzene	112	77, 114
Dibromofluoromethane	113		Dibromochloromethane	129	127
Dichlorodifluoromethane	85	87	Ethylbenzene	91	106
Dichloroethane-d_4	102	65	m-Xylene	106	91
Diethyl ether	74	45, 59	o-Xylene	106	91
Diisopropyl ether	45	102	p-Xylene	106	91
Ethyl acetate (pp)	88	43, 45, 61	Styrene	104	78
Ethyl tert Butyl Ether	59		Tetrachloroethene	164	129,131,166
Freon 113	151				
Iodomethane	142	127, 141	**1,4 Dichlorobenzene-d4**	152	115,150
Isobutyl alcohol (pp)	43	43, 41, 42, 74	1,1,2,2-Tetrachloroethane	83	131, 85
Methacrylonitrile (pp)	41	41, 67, 39, 52, 66	1,2,3-Trichlorobenzene	180	182, 145
Methyl Acetate	43	74	1,2,3-Trichloropropane	75	77
Methylene chloride	84	86, 49	1,2,4-Trichlorobenzene	180	182, 145
Methyl-t-butyl ether	73	57	1,2,4-Trimethylbenzene	105	120
Propionitrile (ethyl cyanide)(pp)	54	54, 52, 55, 40	1,2-Dibromo-3-chloropropane(pp)	75	155, 157
Tetrahydrofuran	42		1,2-Dichlorobenzene	146	111,148
trans-1,2-Dichloroethene	96	61, 98	1,3,5-Trimethylbenzene	105	120
Trichlorofluoromethane	151	101, 153	1,3-Dichlorobenzene	146	111, 148
Vinyl acetate	43	86	1,4-Dichlorobenzene	146	111, 148
Vinyl chloride	62	64	2-Chlorotoluene	91	126
Methyl Acrylate	55	85	4-Bromofluorobenzene	95	174, 176
2,2,4 Trimethylpentane	57				
1-chloro-1, 1-difluoroethane	65	45,85			
1,1,1-trifluoroethane	69	69,45			
1,1-dichloro-1-fluroethane	81	45,61			
2,2-Dichloropropane	77	97,79			
1,4 Difluorobenzene	114	63, 88	4-Chlorotoluene	91	126
1,1,2-Trichloroethane	83	97, 85	Benzyl chloride	91	91, 126, 65, 128
1,1-Dichloropropene	75	110, 77	Bromobenzene	156	77, 158

Table 7. Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)	Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
1,2 Dichloroethane	62	98	Cyclohexanone	55	
1,2 Dichloropropane	63	112	Hexachlorobutadiene	225	223, 227
1,4-Dioxane (pp)	88	88, 58, 43, 57	Hexachloroethane (pp)	201	166, 199, 203
2-Chloroethyl-vinylether (pp)	63	65, 106	Isopropylbenzene	105	120
2 – Hexanone	43	58,57,100	Naphthalene	128	-
2-Hexanone (pp)	43	58, 57, 100	n-Butylbenzene	91	92, 134
2-Nitropropane	46	-	n-Propylbenzene	91	120
3 Methyl –1 butanol	55		Pentachloroethane (pp)	167	167,130,132,165,169
4-Methyl-2-pentanone (pp)	100	43, 58, 85	p-isopropyltoluene	119	134,91
Benzene	78	-	sec-Butylbenzene	105	134
Bromodichloromethane	83	85, 127	tert-Buytlbenzene	119	91, 134
Carbon tetrachloride	117	119	trans-1,4-Dichloro-2-butene (pp)	53	88, 75
cis-1,3-Dichloropropene	75	77, 39			
Methylcyclohexane	83		**(pp) = Poor Purging Efficiency**		

Table 7-1 SIM - Volatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion (s)
Tert Butyl Alcohol-d9		
1,4-Dioxane	88	58
Toluene –d8	98	100
4-BFB	95	174, 176

Table 8. STANDARDS PREPARATION

A) Internal standard and Surrogate mixtures:

	a) 25/250 µg/ml	b) 250/2,500 µg/ml
Internal Standard Mixture (2,000 µg/ml)	1.25 ml	1 .25 ml
Tert Butyl Alcohol-d_9 (50,000 µg/ml)	0.5 ml	0.5 ml
Surrogate Mixture (2,500 µg/ml)	1 ml	1 ml
Methanol	97.25 ml	7.25 ml
Total	100 ml	10 ml

- 25/250 µg /ml internal standard and surrogate mixture: The mixture is prepared by measuring 1.25ml of 2,000 µg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 µg/ml TBA-d_9 (Absolute or equivalent), 1 ml of 2,500 µg /ml Method 8260A Surrogate Standard Mixture (Ultra or equivalent) and bringing to 100 ml with methanol.

- 250/2,500 µg /ml internal standard and surrogate mixture: The mixture is prepared by measuring 1.25 ml of 2,000 µg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 µg/ml TBA-d_9 (Absolute or equivalent), 1 ml of 2,500 µg /ml Method 8260A Surrogate Standard Mixture (Ultra or equivalent) and bringing to 10 ml with methanol.

- 100 µg/ml surrogate mixture: The solution is prepared at 100 µg/ml by measuring 0.4 ml of 2,500 µg/ml Method 8260A Surrogate Standard Mixture (Ultra or equivalent) and bringing to 10 ml with methanol.

- 25/250 µg /ml internal standard mixture: The solution is prepared by measuring 1.25 ml of 2,000 µg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 µg/ml TBA-d_9 (Absolute or equivalent), and bringing to 100 ml with methanol.

- 250/2,500 µg /ml internal standard mixture: The solution is prepared by measuring 1.25 ml of 2,000 µg /ml Internal Standard Mixture (Ultra or equivalent), 0.5 ml of 50,000 µg/ml TBA-d_9 (Absolute or equivalent), and bringing to 10 ml with methanol.

B) Bromofluorobenzene (BFB):

	a) 25 µg/ml	b)) 250 µg/ml
BFB (25,000 µg/ml)	0.1 ml	0.1 ml
Methanol	99.9 ml	9.9 ml
Total	100 ml	10 ml

- 25 µg /ml solution for direct injection: The BFB is prepared at 25 µg /ml by measuring 0.1 ml of 25,000 µg /ml (Absolute Stock or equivalent) and diluting to 100 ml with methanol.

- 250 µg /ml solution for purging: The BFB is prepared at 250 µg /ml by measuring 0.1 ml of 25,000 µg /ml (Absolute Stock or equivalent) and diluting to 10 ml with methanol.

Table 8. STANDARD PREPARATION (Continued)

C) Secondary dilution standards:

2nd Dilution Standards	Stock Solution	Concentration (µg/ml)	Volume Added (µl)	Final Volume in Methanol (ml)	Final Concentration (µg/ml)
V8260 Mixture	EPA Method 524.2 Volatiles	2,000	2,500	50	100
	Acrolein	Neat (90%)	66.2		1,000
	Acrylonitrile*	Neat	25		500+
	Propionitrile**	Neat	58.9		1,000++
	Di-iso Butylene	Neat	7.1		100
	Cyclohexane	Neat	6.5		100
	Cyclohexanone	Neat	52.9		1,000
V8260 Custom Mixture	Custom Volatiles Mix A	2,000	2,500	50	100
	Custom Volatiles Mix B	2,000 -100,000	2,500		100 - 5,000
	Epichlorohydrin	Neat	21.4		500
	Iso-Amyl alcohol	Neat	125		2,000
	2-Chloroethyl vinyl ether	Neat	20.1		500
	Ethyl tert-butyl ether	Neat	6.8		100
	Tert-Amyl methyl ether	Neat	6.56		100
	Benzyl chloride	Neat	4.6		100
Gas Mixture	VOC Gas Mixture	2,000	1,000	20	100

- 100 µg /ml V8260 mixture: The mixture is prepared at 100 µg /ml by measuring 2 ml of 2,000 µg /ml EPA Method 524.2 Volatiles stock standard, appropriate amount of some neat compounds, and bringing to 50 ml with methanol.
  * Acrylonitrile = 400 µg /ml (Neat) + 100 µg /ml (EPA Method 524.2 Volatiles)
  ** Propionitrile = 900 µg /ml (Neat) + 100 µg /ml (EPA Method 524.2 Volatiles)

- 100 µg /ml V8260 custom mixture: The mixture is prepared at 100 - 5,000 µg /ml by measuring 2.5ml of 2,000 µg /ml Custom Volatiles Mix A, 2.5 ml of 2,000 - 100,000 µg/ml Custom Volatiles Mix B, appropriate amount of some neat compounds, and bringing to 50 ml with methanol.

- 100 µg /ml gas mixture ***: The mixture is prepared at 100 µg /ml by measuring 1 ml of 2,000 µg /ml stock standard and bring to 20 ml with methanol.
  ******* Gas mixture should be prepared weekly.

Table 8. STANDARD PREPARATION (Continued)

D).1 Initial Calibration Standards: using DI water bring to 50 ml final volume: all mixtures used should be **secondary dilution** standards at **100 ppm**.

Standard and Surrogate Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)	Surrogate Mix (100ppm)
1 ppb	0.5 µl	0.5 µl	0.5 µl	0.5 µl#
2 ppb *	1.0 µl	1.0 µl	1.0 µl	1.0 µl#
5 ppb	2.5 µl	2.5 µl	2.5 µl	2.5 µl#
10 ppb *	5 µl	5 µl	5 µl	5 µl#
20 ppb	10 µl	10 µl	10 µl	10 µl#
50 ppb	25 µl	25 µl	25 µl	25 µl#
100 ppb	50 µl	50 µl	50 µl	50 µl#
200 ppb	100 µl	100 µl	100 µl	100 µl#
300 ppb *	150 µl	150 µl	150 µl	150 µl#
400 ppb *	200 µl	200 µl	200 µl	200 µl#

* depending upon the instrument.
\# See Section 10.2.2.1 for correction factor.

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of each standard into vial. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

D).2 Initial Calibration Standards for 1,4-Dioxane using SIMS

Standard and Surrogate Concentration (ppb)	1,4-Dioxane Solution (100ppm)	Surrogate Mix (100ppm)	DI Water – Final Volume (ml)
2	2 µl	1 µl	100
5	5 µl	2 µl	100
25	25 µl	5 µl	100
50	25 µl	2.5 µl	50
100	50 µl	5 µl	50
200	100 µl	10 µl	50
400	200 µl	20 µl	50

Table 8. STANDARD PREPARATION (Continued)

E) Continuing Calibration Standard: using DI water bring to 50 ml final volume: All mixtures used are secondary dilution standards at 100 ppm.

Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)
50 ppb	25 µl	25 µl	25 µl

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the continuing calibration standard into vial. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

F) Blank Spike (BS): using DI water bring to 50 ml final volume: All mixtures used are 100 ppm secondary dilution standards.

Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)
50 ppb	25 ul	25 ul	25 ul

For lower detection level required (test code: V8260LL)

Concentration	V8260 Mix (100 ppm)	V8260 Custom Mix (100 ppm)	Gas compound Mix (100 ppm)
20 ppb	10 ul	10 ul	10 ul

- When calibrating for Method 5035 low-level soil samples, add 1g of sodium bisulfate to the 40-ml vial before aliquot 5 ml of the blank spike into vial. This is equivalent to the amount of sodium bisulfate added to the samples and will maintain a consistent purging efficiency of the compounds.

Table 9. GUIDELINE FOR DILUTION PREPARATION

Water Sample

Dilution	Sample amount taken	Final volume A (volumetric)	Take from final volume A	Final volume B (volumetric)
1:2	25 ml	50 ml		
1:5	10 ml	50 ml		
1:10	5 ml	50 ml		
1:20	2.5 ml	50 ml		
1: 25	2 ml	50 ml		
1:50	1 ml	50 ml		
1:100	0.5 ml	50 ml		
1:200	250 µl	50 ml		
1:250	200 µl	50 ml		
1:500	100 µl	50 ml		
1:1000	50 µl	50 ml		
1:2000	25 µl	50 ml		
1:2500	20 µl	50 ml		
1:5000	10 µl	50 ml		
1:10000	0.5 ml	50 ml	0.5 ml	50 ml
1:20000	0.5 ml	50 ml	250 µl	50 ml
1:25000	0.5 ml	50 ml	200 µl	50 ml
1:50000	0.5 ml	50 ml	100 µl	50 ml
1:100000	0.5 ml	50 ml	50 µl	50 ml

Soil-Low level (Non-Encore sample)

Dilution	Sample amount taken	Final volume
1:2	2.5 gram	5 ml
1:5	1 gram	5 ml
1:10	0.5 gram	5 ml

Soil-medium level

Additional Dilution	Sample in Methanol amount taken	Final volume (volumetric)
1:1	1 ml	50 ml
1:2	0.5 ml	50 ml
1:5	200 µl	50 ml
1:10	100 µl	50 ml
1:20	50 µl	50 ml
1: 25	40 µl	50 ml
1:50	20 µl	50 ml
1:100	10 µl	50 ml
1:200	5 µl	50 ml
1:250	4 µl	50 ml
1:500	2 µl	50 ml

Table 10. REPORTING LIMITS

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Chlorodifluoromethane	5	5	Chloroform	5	5
Dichlorodifluoromethane	5	5	Freon 113	5	5
Chloromethane	5	5	Methacrylonitrile	10	10
Vinyl chloride	5	5	Butyl Acetate	5	5
Bromomethane	5	5	1,1,1-Trichloroethane	5	5
Chloroethane	5	5	Heptane	5	5
Trichlorofluoromethane	5	5	n-Propyl acetate	5	5
Ethyl ether	5	5	2-Nitropropane	10	10
Acrolein	50	50	Tetrahydrofuran	10	10
1,1-Dichloroethene	2	2	2-Chloroethyl Vinyl Ether	20	20
Tertiary butyl alcohol	50	50	n-Butyl alcohol	250	250
Acetone	5	5	Cyclohexane	5	5
Methyl acetate	5	5	Carbon Tetrachloride	1	1
Allyl chloride	5	5	1,1-Dichloropropene	5	5
Acetonitrile	100	100	Isopropyl Acetate	5	5
Iodomethane	25	25	Benzene	1	1
Iso-butyl alcohol	50	50	1,2-Dichloroethane	2	2
Carbon disulfide	5	5	Trichloroethene	1	1
Methylene chloride	2	2	Methyl methacrylate	10	10
Methyl tert butyl ether	1	1	1,2 Dichloropropane	1	1
Trans-1,2-Dichloroethene	5	5	Di-isobutylene	5	5
Di-isopropyl ether	5	5	Dibromomethane	5	5
2-Butanone	5	5	1,4 Dioxane	125	125
1,1-Dichloroethane	2	2	Bromodichloromethane	1	1
Hexane	5	5	cis-1,3-Dichloropropene	1	1
Chloroprene	5	5	4-Methyl-2-pentanone	5	5
Acrylonitrile	5	5	Toluene	1	1
Vinyl acetate	10	10	trans-1,3-Dichloropropene	1	1
Ethyl acetate	5	5	Ethyl methacrylate	10	10
2,2-Dichloropropane	5	5	1,1,2-Trichloroethane	3	3
Cis-1,2-Dichloroethene	5	5	2-Hexanone	5	5
Bromochloromethane	5	5	Cyclohexanone	5	5

Table 10. REPORTING LIMITS (Continued)

Compound	Water	Soil	Compound	Water	Soil
	µg/l	µg/kg		µg/l	µg/kg
Tetrachloroethene	1	1	4-Chlorotoluene	5	5
1,3-Dichloropropane	5	5	1,3,5-Trimethylbenzene	5	5
Dibromchloromethane	5	5	tert-Butylbenzene	5	5
1,2-Dibromoethane	2	2	1,2,4 Trimethylbenzene	5	5
Chlorobenzene	2	2	sec-Butylbenzene	5	5
1,1,1,2-Tetrachloroethane	5	5	1,3-Dichlorobenzene	5	5
Ethylbenzene	1	1	p-Isopropyltoluene	5	5
M,p-Xylene	1	1	1,4-Dichlorobenzene	5	5
o-Xylene	1	1	1,2-Dichlorobenzene	5	5
Styrene	5	5	n-Butylbenzene	5	5
Bromoform	4	4	1,2-Dibromo-3-choropropane	10	10
Isopropylbenzene	2	2	1,2,4-Trichlorobenzene	5	5
Bromobenzene	5	5	Hexachlorobutadiene	5	5
1,1,2,2-Tetrachloroethane	2	2	Naphthalene	5	5
Trans-1,4-Dichloro-2-butene	5	5	1,2,3-Trichlorobenzene	5	5
1,2,3-Trichloropropane	5	5	Epichlorohydrin	100	100
n-Proplybenzene	5	5	3-Methyl-1-butanol	5	5
2-Chlorotoluene	5	5	Hexachloroethane	5	5
Ethanol	50	--	Methyl Acrylate	5	--
Benzyl Chloride	1	--	Methylcyclohexane	5	5
2,2,4 Trimethylpentane	5	5	1,1,1 trifluoroethane	5	10
1-chloro-1,1-difluoroethane	5	10	1,1-dichloro-1-fluoroethane	5	10

Table 11. COMPOUNDS THAT MAY EXHIBIT CARRYOVER

Compound
1,2,4-Trichlorobenzene
Hexachlorobutadiene
Naphthalene
1,2,3-Trichlorobenzene

4. $\delta^{34}S$ & $\delta^{18}O$ (Sulfur and Oxygen Isotope Analysis) of Dissolved Sulfate

Equipment and Supplies

Thermo Delta V Plus
Mettler Toledo MX5 Ultra-Microbalance
Elementar Vario EL
Thermo TC/EA
Thermo ConFlo II
Thermo AQUAFast II ™ Colorimeter
0.45 micron nylon filter
1N HCl
$BaCl_2$ solution
Filtering apparatus
Various sized beakers
Drying oven
Petri dishes
Tin boats
Silver boats

Method/Procedure The $\delta^{34}S$ & $\delta^{18}O$ of dissolved sulfate is determined by the barium sulfate precipitation technique. Prior to preparation the sulfate concentration must be obtained from the client or determined using a Thermo AQUAFast II ™ colorimeter; a minimum sulfate concentration of 5ppm is required for this analysis. Once the sulfate concentration is known, the amount of sample needed to obtain 25mg of barium sulfate is weighed into a clean beaker. Samples are then filtered to remove particulate matter before being brought to a boiling temperature. Calcium carbonate in the sample is removed by adding 1N hydrochloric acid until the sample reaches a pH of 1-3. An appropriate amount of barium chloride solution is added based on the concentration of sulfate in the sample. The reaction is given sufficient time to complete under heat; a testing solution is used to ensure that all dissolved sulfate has precipitated. The precipitant is then filtered and dried, the final amount is weighed.

The $\delta^{34}S$ of the dried barium sulfate is then determined by combustion to SO_2 gas using an Elementar Vario EL EA. Approximately 1.2mg $BaSO_4$ is weighed into a tin capsule and loaded into an autosampler. The sample is then combusted and passed over a reduction furnace. The resulting SO_2 gas is passed through a ConFlo II interfaced to the IRMS, where it is compared against a reference gas.

Analysis of $\delta^{18}O$ is performed using a Thermo TC/EA. Approximately 300 micrograms of $BaSO_4$ is weighed into silver boats and placed in a zero blank autosampler. The sample is thermally converted to CO gas in the EA furnace. The CO gas is introduced into the IRMS through a ConFlo II interface. Sample values are referenced against international standards.

Maintenance Glassware is washed and rinsed with deionized water to remove residual $BaSO_4$.

QA/QC At a minimum, every tenth sample preparation is a duplicate. Approximately every tenth EA/TCEA analysis a set of standards is analyzed after every ten samples, along with at least one check standard per analysis run.

Calculation Calculations are performed by the software on the IRMS (Isotope Ratio Mass Spectrometer) at the time of analysis. Data normalization against primary international standards is performed using Microsoft Excel.

Documentation All records of sample preparation and notes are hand written in bound log books. All sample data including the date prepared are stored electronically and in print.

Sample Handling Samples should be collected and stored at 4°C until analyzed. Samples should be shipped overnight in a cooler on ice. Filtering prior to shipment is preferred but is not required.

X-Ray Diffraction Lab Method
Bulk & Clay Fraction Analysis
of Soil and Rock Samples

Mineralogy, Inc. observes the following methodology for our routine bulk and clay x-ray diffraction analysis of soil and rock samples. Following arrival of the samples at the laboratory, a (representative) five gram portion of the specimen will be split from the bulk rock or soil samples for each of the intervals submitted for analysis. If evidence of oil staining is present, the samples will then be extracted with toluene to remove the hydrocarbons and dried at 60 degrees Centigrade. Each of the samples will be subsequently split into two equal portions to provide material for the bulk and clay fraction analysis respectively. The "bulk" sample splits are ground in a high Cr-steel milling device to yield powders with a mean particle diameter of approximately 20-30 micrometers.

The sample splits reserved for clay fraction preparation are placed in centrifuge tubes and mixed with approximately 40mL of de-ionized water. The suspensions are then dispersed with ultrasonic energy for 5 minutes and centrifuged at 2000RPM for 10 minutes, following which the uppermost 2mL of suspension is decanted and transferred to glass slides. The slides are dried at 40 degrees Centigrade to yield oriented clay mounts with a particle size of less than 4 micrometers.

The bulk powders and oriented clay mounts are then scanned with a Rigaku Mini Flex X-ray diffractometer using copper K-alpha radiation. Operating parameters are noted as follows: generator power settings: 40 kV, 20 mA, Receiving optics: receiving slit, Soller slit, scattering slit, and SC70 detector, Incident optics: divergence slit, and incident parallel slit, and an ASC6 sample changer. The standard scanning parameters for a bulk XRD specimen are from 3° 2-theta to 50° 2-theta. The step size is 0.020° 2-Theta and the dwell time at each step is 0.3 seconds. The air-dried oriented clay slides are scanned from 3-26 degrees 2-Theta. The clay mounts are then suspended in a sealed jar containing ethylene-glycol for a period of 8 hours. The ethylene-glycol-solvated clay mounts are then analyzed with a scan range of 3-26 degrees 2-Theta. The procedures outlined above will provide the "raw" digital data (scan intensity vs. degrees 2-Theta) used to graph the bulk, air-dried clay and ethylene glycol solvated clay diffractograms.

Computer analysis of the diffractograms provides for identification and semi-quantitative analysis of the relative abundance of the various mineral phases. Rigaku's PDXL2 (2012) software and the ICDD JCPDS mineral database, with over 600,000 known compounds, are used to identify mineral phases present.

The XRD methodology outlined above is adapted from the following reference:

Moore, D.M. and Reynolds, R.C.Jr., 1989, X-ray Diffraction and the Identification of Clay Minerals, 332p., Oxford University