



de maximis, inc.

200 Day Hill Road
Suite 200
Windsor, CT 06095
(860) 298-0541
(860) 298-0561 Fax

October 19, 2004

Ms. Melissa Taylor
US EPA, Region 1
OSRR, MA Superfund Section
One Congress Street, Suite 1100
Mail Code HBO
Boston, MA 02114-2023

**Subject: RI/FS Work Plan Modification Request No.1
Nuclear Metals, Inc. Site
Concord, Massachusetts**

Dear Ms. Taylor:

This letter documents the first change to the Final Quality Assurance Project Plan (QAPP) and Final Field Sampling Plan (FSP) for the Nuclear Metals Superfund Site in Concord, Massachusetts in accordance with Section 4.2.1 – “Modifications to Approved QAPP” of the Final QAPP (September 29, 2004),.

This request for modification to the Work Plans addresses the following issues:

1. Review of the QAPP and FSP by the project team prior to initiation of the AOI 1 - Holding Basin soil borings revealed inconsistency in the between the number of samples and types of analyses to be performed for FS parameters. The team recommends 22 total samples be collected for FS parameter analysis, instead of the 96 proposed in the FSP. In addition, the list of proposed parameters has been revised to consist of soil alkalinity, pH, TOC, and calcium. FSP Tables 3.1.2, 3.1.3, and QAPP Table 8.01 have been revised to reflect these proposed changes. Laboratory procedures for performance of the pH and soil alkalinity methods are attached. These changes do not reduce the number of soil samples planned for characterization of nature and extent of impact (i.e., VOCs, SVOCs, radiological parameters, TAL metals, specialty metals, etc.) nor do they reduce the number of planned soil borings.

2. The May 19, 2004 EPA comment 3-41 on the Draft Work Plans recommended that soil borings be analyzed for nitrate from AOIs that are potential sources of the nitrate contamination identified in the groundwater. Based on the location of the nitrate groundwater plume and the history of operations at the facility, AOI 1 - Holding Basin is presumably the source of the groundwater nitrate plume. Therefore, Tables 3.1.3 of the FSP and 8.0.1 of the QAPP have been updated to reflect the addition of nitrate analyses in soils to the AOI 1 - Holding Basin borings.
3. As a result of Department of Transportation shipping regulations which became effective October 2004, the proposed laboratory (Woods Hole Group) for the AVS:SEM analyses can no longer accept samples with a potential for radiological contamination. Therefore, we propose using Southwest Research Institute in San Antonio, Texas to perform the AVS:SEM analyses. Tables 6.1.3 and 12.0.1 of the QAPP have been revised to reflect the proposed changes, and the laboratory SOP is attached.

The following revised or additional files are included as attachments to this request for modifications:

- FSP Table 3.1.2 (proposed changes are highlighted in yellow)
- FSP Table 3.1.3 (proposed changes are highlighted in yellow)
- QAPP Table 6.1.3 (proposed changes are highlighted in yellow)
- QAPP Table 8.0.1 (proposed changes are highlighted in yellow)
- QAPP Table 12.0.1 (proposed changes are highlighted in yellow)
- Soil Alkalinity using the EPA (Sobek) Method
- Laboratory SOP for soil pH
- Laboratory SOP for AVS:SEM

Soil borings and related soil sampling are planned to commence at the Holding Basin on Monday, October 25, 2004. Please contact me if you have any questions.

Sincerely,



Bruce Thompson
Project Coordinator

Enclosures

cc: Bob Ciancirulo, US EPA
Daniel Keefe, MADEP
Ed Conroy, Metcalf & Eddy

**Table 3.1.2
AOI 1 - Holding Basin
Summary of Planned RI Sampling Program**

**Field Sampling Plan
Nuclear Metals, Inc.
Concord, Massachusetts**

Exploration Type	Exploration ID	Location	Depth	Rationale
Soil Borings through Holding Basin Floor				
Soil	SB-RI-01001 to SB-RI-01003	Three of six proposed borings through basin floor	BOB at top of rock. Soil characterization samples every 5 ft; Analytical samples as specified in text.	Characterize nature and extent of impact from uranium and other COCs and provide data for feasibility study of remediation alternatives
Soil	SB-RI-01004 to SB-RI-01006	Three of six proposed borings through basin floor	BOB at top of till. Soil characterization samples every 5 ft; Analytical samples as specified in text.	Characterize nature and extent of impact from uranium and other COCs and provide data for feasibility study of remediation alternatives
Soil Borings around Holding Basin Rim				
Soil	SB-RI-01007 to SB-RI-01014	Eight of 16 proposed borings positioned outside of basin.	BOB at top of rock. Soil characterization samples every 5 ft; Analytical samples as specified in text.	Characterize nature and extent of impact from uranium and other COCs and provide data for feasibility study of remediation alternatives
Soil	SB-RI-01015 to SB-RI-01022	Eight of 16 proposed borings positioned outside of basin.	BOB at 10 ft bgs.	Provide additional density of shallow data for risk assessment and provide data for feasibility study of remediation alternatives.
Groundwater	No new wells are planned within AOI 1; see Section 3.16 for description of new and existing wells that will characterize and monitor groundwater migrating from the vicinity of the Holding Basin			

Notes:

AOI = Area Of Investigation

COC - contaminant of concern

ID = identification

ft = feet

BOB = bottom of boring

**Table - 3.1.3 Rev 1
AOI 1 - Holding Basin
Analytical Program Summary**

**Field Sampling Plan
Nuclear Metals, inc.
Concord, Massachusetts**

Sample Location ID	Specialty Metals	TAL Metals	Nitrate	Uranium and Thorium Isotopes	HTDR	VOCs	SVOCs	PAHs	On-Site PCBs	PCBs	EPH	FS Parameters	Fluoride
Analytical Method:	6020	6020/7471A	9056	Alpha Spec	Various	8260B	8270C	8310	Immuno-assay	8082	MADEP	Various	9056
RI Characterization Samples													
<i>Soil - Borings Through Basin Floor</i>													
SB-RI-01001 to SB-RI-01003	30	30	30	6	3	3	3	3	-	3	3	4	3
SB-RI-01004 to SB-RI-01006	21	21	21	6	3	3	3	3	-	3	3	-	
<i>Soil - Borings Around Basin Rim</i>													
SB-RI-01007 to SB-RI-01014 (10 ft intervals)	80	80	80	16	0	8	8	8	-	8	8	15	
SB-RI-01015 to SB-RI-01022 (3 shallow intervals)	24	24	24	8	0	8	8	8	-	8	8	3	
<i>Groundwater</i>													
See Section 3.16 for Sitewide Groundwater Program													
Total Soil	155	155	155	36	6	22	22	22	0	22	22	22	3

Notes:

AOI = area of investigation

ID = identification

Specialty metals include uranium, thorium, molybdenum, titanium, tungsten, and zirconium.

VOCs = volatile organic compounds

TAL = target analyte list

HTDR includes Am-241, Cm-243/244/245/246, Np-237, Pu-237/238/239/240/241/242, Sr-90, Tc-99, U-236

SVOCs = semivolatile organic compounds

PCBs = polychlorinated biphenyls

EPH = extractable petroleum hydrocarbons

FS Parameters include: soil alkalinity, pH, TOC, calcium

Proposed groundwater sampling locations by AOI are presented in Table 3.16.2

Proposed groundwater analytical program is presented in Table 3.16.3.

See QAPP Table 6.1.3 and Table 9.2.1 for analytical methods, sample container and preservation requirements.

See FSP Table 3.0.1 for field QC sample collection frequency.

Assumptions used to develop number of analytical samples shown above:

basin floor elev = 160 (not known precisely)

rim ground surface = 178

water table = 138

till surface = 110 (used 25 ft saturated sands)

bedrock = 94 (used 15 feet till thickness)

**TABLE 6.1.3
 ANALYTICAL SERVICES SUMMARY**

Medium	Analytical Parameter	Proposed in RI/FS	Concentration Level	Analytical Method	SOP ¹	Holding Time and Preservation	Data Package Turnaround Time	Laboratory/Organization (Name and Address: Contact Person and Telephone Number)
Aqueous	TCL VOCs	*	Low	5030/8260B	GL-OA-E-028	14 days HCL, pH<2, zero headspace, 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	TCL SVOCs	*	Low	3510C/8270C	GL-OA-E-009	Extract within 7 days, analyze within 40 days 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	TCL PAHs	*	Low	3510C/8310	GL-OA-E-030	Extract within 7 days, analyze within 40 days 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	TAL Metals, excluding calcium, potassium and sodium	*	Low	3005A/6020/7470A (Hg)	GL-MA-E-014	6 months (28 days for Hg) HNO ₃ , pH<2	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171

**TABLE 6.1.3
 ANALYTICAL SERVICES SUMMARY**

Medium	Analytical Parameter	Proposed in RI/FS	Concentration Level	Analytical Method	SOP ¹	Holding Time and Preservation	Data Package Turnaround Time	Laboratory/Organization (Name and Address: Contact Person and Telephone Number)
Aqueous	Specialty Metals (molybdenum, thorium, titanium, tungsten, uranium and zirconium)	*	Low	3005A/6020	GL-MA-E-014	6 months HNO ₃ , pH<2	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	Hardness, Total as CaCO ₃	*	Low	SM2340B	GL-GC-E-025	6 months HNO ₃ , pH<2, 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	TOC	*	Low	415.1	GL-GC-E-062	28 days H ₂ SO ₄ , pH<2, zero headspace, 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	Gamma Emitting Radionuclides	*	Low/Medium	Gamma Spectroscopy	GL-RAD-A-013	6 months HNO ₃ , pH<2	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171

**TABLE 6.1.3
 ANALYTICAL SERVICES SUMMARY**

Medium	Analytical Parameter	Proposed in RI/FS	Concentration Level	Analytical Method	SOP ¹	Holding Time and Preservation	Data Package Turnaround Time	Laboratory/Organization (Name and Address: Contact Person and Telephone Number)
Aqueous	Uranium and Thorium Isotopes	*	Low/Medium	Alpha Spectroscopy	GL-RAD-A-011	6 months HNO ₃ , pH<2	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	Hard to Detect Radionuclides	*	Low/Medium	Various (Gas Flow, Liquid Scintillation, Gamma Spectroscopy)	GL-RAD-A-032 GL-RAD-A-035 GL-RAD-A-004 GL-RAD-A-005	6 months HNO ₃ , pH<2	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	Ferrous Iron	*	Low	SM 3500 – Fe-D	GL-GC-E-099	HCL, 4°C 24 hours	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	Ferric Iron	*	Low	SM 3500 – Fe-D	GL-GC-E-099 GL-GC-E-014	HCL, 4°C 24 hours	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171

**TABLE 6.1.3
 ANALYTICAL SERVICES SUMMARY**

Medium	Analytical Parameter	Proposed in RI/FS	Concentration Level	Analytical Method	SOP ¹	Holding Time and Preservation	Data Package Turnaround Time	Laboratory/Organization (Name and Address: Contact Person and Telephone Number)
Aqueous	Sulfide	*	Low	EPA 376.2/HACH 8131	GL-GC-E-052	7 days Zinc acetate and NaOH to pH>9, 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	Sulfate, Nitrite, Nitrate, Fluoride	*	Low	EPA 300.0 or SW846 9056	GL-GC-E-086	48 hours for Nitrate & Nitrite, 28 days for Sulfate and Fluoride 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	Hexavalent Chromium		Low/Medium	7196A	GL-GC-E-044	24 hours 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Aqueous	EPH	*	Low	MADEP 8015/8270	ORG 71 (prep) and ORG 74	Extract within 14 days, analyze within 40 days HCL, pH<2, 4°C	21 Days	General Engineering Laboratories of Ohio, LLC 6954 Cornell Road Suite 300 Cincinnati, OH 45242 Mr. Erik Corbin 513*489*2001

**TABLE 6.1.3
 ANALYTICAL SERVICES SUMMARY**

Medium	Analytical Parameter	Proposed in RI/FS	Concentration Level	Analytical Method	SOP ¹	Holding Time and Preservation	Data Package Turnaround Time	Laboratory/Organization (Name and Address: Contact Person and Telephone Number)
Aqueous	TCLP		Low	1311	GL-LB-E-006	Metals: If less than 5% solids, analyze within 6 months (28 days for Hg) VOCs: If less than 5% solids, analyze within 14 days SVOC, Pest/PCBs: If less than 5% solids, extract within 7 days, analyze within 40 days 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	TCL VOCs	*	Low	5035/8260B	GL-OA-E-026	Freeze within 48 hours, analyze within 14 days 5-mL di water, 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171

**TABLE 6.1.3
 ANALYTICAL SERVICES SUMMARY**

Medium	Analytical Parameter	Proposed in RI/FS	Concentration Level	Analytical Method	SOP ¹	Holding Time and Preservation	Data Package Turnaround Time	Laboratory/Organization (Name and Address: Contact Person and Telephone Number)
Solid	TCL SVOCs	*	Low/Medium	3350/8270C	GL-OA-E-009	Extract within 14 days, analyze within 40 days 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	TCL PAHs	*	Low/Medium	3350/8310	GL-OA-E-030	Extract within 14 days, analyze within 40 days 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	TAL Metals, excluding potassium and sodium	*	Low/Medium	3050A/6020/7471A (Hg)	GL-MA-E-014	6 months (Hg 28 days) 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	Specialty Metals (molybdenum, thorium, titanium, tungsten, uranium and zirconium)	*	Low/Medium	3050A/6020	GL-MA-E-014	6 months 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171

**TABLE 6.1.3
 ANALYTICAL SERVICES SUMMARY**

Medium	Analytical Parameter	Proposed in RI/FS	Concentration Level	Analytical Method	SOP ¹	Holding Time and Preservation	Data Package Turnaround Time	Laboratory/Organization (Name and Address: Contact Person and Telephone Number)
Solid	SPLP Metals		Medium	1312/6020	GL-LB-E-024	Leach within 28 days; analyze within 6 months (28 days for Hg) 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	AVS:SEM	*	Low/Medium	AVS:SEM in sediment	TAP-01-0406-023	14 days 4°C	21 Days	Southwest Research Institute 6220 Culebra Road San Antonio, TX 78238 Mr. Herb Schattenberg
Solid	Grain size		N/A	ASTM D422	ASTMD422 – Method Followed (no SOP)	None	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	TOC	*	Low/Medium	9060	GL-GC-E-062	28 days 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	Fluoride, Nitrate, Nitrite	*	Low	EPA 300.0 or SW846 9056	GL-GC-E-086	48 hours for Nitrate & Nitrite, 28 days for Fluoride 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171

**TABLE 6.1.3
 ANALYTICAL SERVICES SUMMARY**

Medium	Analytical Parameter	Proposed in RI/FS	Concentration Level	Analytical Method	SOP ¹	Holding Time and Preservation	Data Package Turnaround Time	Laboratory/Organization (Name and Address: Contact Person and Telephone Number)
Solid	Soil Alkalinity	*	Low	EPA (Sobek)	EPA (Sobek)	14 days, 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	pH	*	N/A	9045	GL-GC-E-008	Upon arrival, 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	EPH	*	Low/Medium	MADEP/8015/8270	ORG 79 (prep) and ORG 80	Extract within 14 days, analyze within 40 days 4°C	21 Days	General Engineering Laboratories of Ohio, LLC 6954 Cornell Road Suite 300 Cincinnati, OH 45242 Mr. Erik Corbin 513*489*2001
Solid	PCBs	*	Low/Medium	3550B/8082	GL-OA-E-040	Extract within 14 days, analyze within 40 days 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171

**TABLE 6.1.3
 ANALYTICAL SERVICES SUMMARY**

Medium	Analytical Parameter	Proposed in RI/FS	Concentration Level	Analytical Method	SOP ¹	Holding Time and Preservation	Data Package Turnaround Time	Laboratory/Organization (Name and Address: Contact Person and Telephone Number)
Solid	Gamma Emitting Radionuclides	*	Low/Medium	Gamma Spectroscopy	GL-RAD-A-013	6 months	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	Uranium and Thorium Isotopes	*	Low/Medium	Alpha Spectroscopy	GL-RAD-A-011	6 months	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	Hard to Detect Radionuclides	*	Low	Various (Gas Flow, Liquid Scintillation, Gamma Spectroscopy)	GL-RAD-A-032 GL-RAD-A-035 GL-RAD-A-004 GL-RAD-A-005	6 months	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171

**TABLE 6.1.3
 ANALYTICAL SERVICES SUMMARY**

Medium	Analytical Parameter	Proposed in RI/FS	Concentration Level	Analytical Method	SOP ¹	Holding Time and Preservation	Data Package Turnaround Time	Laboratory/Organization (Name and Address: Contact Person and Telephone Number)
Solid	TCLP	*	Low	1311	GL-LB-E-006	Leach within 14 days, except metals which are 28 days VOC: 14 days SVOC, PEST/PCBs: extract within 7 days; analyze within 40 days; Inorganics: 6 months (28 days for Hg) 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Solid	Hexavalent Chromium		Low	7196A	GL-GC-E-044	Extract within 30 days and analyze within 7 days 4°C	21 Days	General Engineering Laboratories, LLC 2040 Savage Road Charleston, SC 29417 Ms. Edie Kent 843*556*8171
Soil Vapor	VOCs		Low	TO-14	Proprietary	14 days	21 Days	Air Toxics LTD 180-B Blue Ravine Road Folsom, CA 95630 Ms. Dede Dodge 800*985*5955

NOTES:

TABLE 6.1.3
ANALYTICAL SERVICES SUMMARY

VOCs = Volatile Organic Compounds
TICs = tentatively identified compounds
SVOCs = semivolatile organic compounds
EPH = extractable petroleum hydrocarbons
PCBs = polychlorinated biphenyls
PAHs = polynuclear aromatic hydrocarbons
TOC = total organic carbon
TCL = target compound list
TAL = target analyte list
TCLP = toxicity characteristic leaching procedure
SPLP = synthetic precipitation leaching procedure
AVS:SEM = acid volatile sulfide:simultaneously extractable metals

**TABLE 8.0.1
ANALYTICAL PROGRAM SUMMARY**

Title: NMI RI/FS QAPP
Revision No.: 1
Revision Date: 10/15/04

Analysis: Method:	Specialty Metals	TAL Metals 6020/7470A/74 71A	Uranium and Thorium isotopes (alpha spec)	HTDRs	VOCs	SVOCs	PAHs	On-Site PCBs by Immuno- assay Test	PCBs	EPH	Feasibility Parameters (see notes below)	AVS/SEM	Fluoride	Nitrate
	6020		Alpha Spec	Various	8260B	8270C	8310	On-Site	8082	MADEP	Various	EPA 1991	9056	9056
Area of Investigation AOI 1 - Holding Basin Soil Samples	155	155	36	6	30	30	30	0	30	30	22	0	3	155
AOI 2 - Drum Burial Area See Table 3.2.3 of FSP														
AOI 3 -Old Landfill Soil Samples	60	60	12	0	60	60	60	0	60	0	0	0	0	0
AOI 4 - Cooling Water Recharge Pond Soil Samples Surface Water samples Sediment samples	37 7 24	37 7 24	7 2 5	0 0 0	37 7 24	37 7 24	37 7 24	0 0 0	0 0 0	37 7 24	0 0 0	0 0 5	0 0 0	0 0 0
AOI 5 - Septic Fields Soil Samples	50	50	8	0	50	50	50	0	0	0	0	0	0	0
AOI 6 - Sphagnum Bog Surface Water samples Sediment samples	11 72	11 72	4 16	0 2	11 58	11 58	11 58	0 0	11 58	11 58	0 0	0 5	0 0	0 0
AOI 7 - Former Waste Storage Area Soil Samples	62	62	14	0	62	62	62	0	0	62	0	0	0	0
AOI 8 - Sweepings and Fill Area Soil Samples	32	32	7	0	32	32	32	0	32	32	0	0	0	0
AOI 9 - Pavement Drain Outfalls Soil Samples Sediment Samples	36 5	36 5	9 5	0 0	0 0	36 5	36 5	0 0	0 0	0 0	0 0	0 0	0 0	0 0
AOI 10 - Northeast Wetland Sediment samples	12	12	2	0	12	12	12	0	0	12	0	3	0	0
AOI 11 - Drain Line Area Soil Samples	40	40	7	0	40	40	40	0	0	40	0	0	0	0
AOI 12 - UST Area Soil Samples	0	0	0	0	0	0	0	0	0	4	0	0	0	0
AOI 13 - Site Structures Building Samples (see Table 3.13.3 of FSP)														
AOI 14 - Surface Soils (On-Site) Soil Samples	77	77	15	0	0	0	0	0	0	0	0	0	0	0
AOI 15 - Transformer Pads Soil Samples	0	0	0	0	0	0	0	24	24	24	0	0	0	0

**TABLE 8.0.1
ANALYTICAL PROGRAM SUMMARY**

Title: NMI RI/FS QAPP
Revision No.: 1
Revision Date: 10/15/04

Analysis: Method:	Specialty Metals	TAL Metals 6020/7470A/74 71A	Uranium and Thorium isotopes (alpha spec)	HTDRs	VOCs	SVOCs	PAHs	On-Site PCBs by Immuno- assay Test	PCBs	EPH	Feasibility Parameters (see notes below)	AVS/SEM	Fluoride	Nitrate
	6020		Alpha Spec	Various	8260B	8270C	8310	On-Site	8082	MADEP	Various	EPA 1991	9056	9056
AOI 16 - Groundwater (Sitewide) Groundwater samples	99	99	20	0	99	99	99	0	0	0	18	0	16	99
AOI 17 -Background Areas (Off-Site)														
Soil Samples	30	30	30	0	0	15	15	0	0	0	0	0	0	0
Groundwater samples	20	20	20	0	0	0	0	0	0	0	0	0	0	0
Surface Water samples	30	30	0	0	10	0	0	0	0	0	0	0	0	0
Sediment samples	45	45	45	0	10	35	35	0	0	0	0	12	0	0
AOI 18 -Assabet River														
Surface Water samples	22	22	5	0	22	0	0	0	0	0	0	0	0	0
Sediment samples	22	22	5	0	22	0	0	0	0	0	0	5	0	0
SUBTOTAL SOIL SAMPLES	607	587	145	6	311	362	362	24	146	229	96	0	3	0
QA/QC SOIL (5% dup, 5% MS, 5% MSD)	93	90	24	3	48	57	57	6	24	36	15	0	0	0
TOTAL SOIL	700	677	169	9	359	419	419	30	170	265	111	0	0	0
SUBTOTAL SURFACE WATER SAMPLES¹	70	70	11	0	50	18	18	0	11	18	0	0	0	0
QA/QC SOIL (5% dup, 5% MS, 5% MSD)	12	12	3	0	9	3	3	0	3	3	0	0	0	0
TOTAL SURFACE WATER	82	82	14	0	59	21	21	0	14	21	0	0	0	0
SUBTOTAL SEDIMENT SAMPLES	180	180	78	2	126	134	134	0	58	94	0	30	0	0
QA/QC SOIL (5% dup, 5% MS, 5% MSD)	30	30	12	3	21	21	21	0	9	15	0	6	0	0
TOTAL SEDIMENT	210	210	90	5	147	155	155	0	67	109	0	36	0	0
SUBTOTAL GROUNDWATER SAMPLES	119	119	40	0	99	99	99	0	0	0	18	0	16	99
QA/QC SOIL (5% dup, 5% MS, 5% MSD)	18	18	9	0	15	15	15	0	0	0	3	0	3	15
TOTAL GROUNDWATER	137	137	49	0	114	114	114	0	0	0	21	0	19	114

Notes:

AOI = area of interest

ID = identification

Specialty metals include uranium, thorium, molybdenum, titanium, tungsten, and zirconium.

TAL = target analyte list

FS Parameters for soil include: soil alkalinity, pH, TOC, and calcium.

FS parameters for groundwater include: TOC, alkalinity, pH, calcium, sulfate, sulfide, ferrous and ferric iron, nitrite, and hardness (as CaCO3).

HTDR includes Am-241, Cm-243/244/245/246, Np-237, Pu-237/238/239/240/241/242, Sr-90, Tc-99, U-236

VOCs = volatile organic compounds

SVOCs = semivolatile organic compounds

PAHs = polynuclear aromatic hydrocarbons

PCBs = polychlorinated biphenyls

EPH = extractable petroleum hydrocarbons

1 = surface water samples will be tested for total and dissolved metals, hardness, and TSS.

**TABLE 12.0.1
FIXED LABORATORY ANALYTICAL METHOD/SOP REFERENCE**

Fixed Laboratory Performing Analysis	Standard Operating Procedure (SOP)	Code	Analytical Parameter	Instrument	Modified for Project Work Y or N
GEL	Synthetic Precipitation Leaching Procedure	GL-LB-E-024	SPLP Metals	N/A	N
GEL	Toxicity Characteristic Leaching Procedure Preparation	GL-LB-E-006	TCLP	None	N
GEL	Sample Receipt, Login, and Storage	GL-SR-E-001	N/A	N/A	N
GEL	Preparation Of Samples For Massachusetts Method Extractable Petroleum Hydrocarbons (EPH)	ORG 71	EPH	FID or GC/MS	N
GEL	Massachusetts Method For The Determination Of Extractable Petroleum Hydrocarbons (EPH)	ORG 74	EPH	FID or GC/MS	N
GEL	Semivolatile Analysis by Gas Chromatography/Mass Spectrometer	GL-OA-E-009	TCL SVOCs	GC/MS	N
GEL	Extraction of Semivolatile and Nonvolatile Organic Compounds from soil, sludge, and other miscellaneous samples	GL-OAE-010	TCL SVOCs	N/A	N
GEL	Extraction of Semivolatile and Nonvolatile Organic Compounds from groundwater, wastewater, and other aqueous samples	GL-OA-E-013	TCL SVOCs	N/A	N
GEL	Volatile Organic Compounds by Gas Chromatograph/Mass Spectrometer	GL-OA-E-038	TCL VOCs	GC/MS	Y – 10 mL purge for low level waters

**TABLE 12.0.1
FIXED LABORATORY ANALYTICAL METHOD/SOP REFERENCE**

Fixed Laboratory Performing Analysis	Standard Operating Procedure (SOP)	Code	Analytical Parameter	Instrument	Modified for Project Work Y or N
GEL	Polynuclear Aromatic Hydrocarbons by HPLC	GL-OA-E-030	TCL PAHs	GC/MS	N
GEL	Polychlorinated Biphenyls	GL-OA-E-040	PCBs	GC/ECD	N
GEL	Organochlorine Pesticides	GL-OA-E-041	Pesticides	GC/ECD	N
GEL	Chloronoxo Acid Herbicides	GL-OA-E-011	Herbicides	GC/ECD	N
GEL	Acid Digestion of Total Metals in Aqueous Samples and Extracts for Analysis by ICP or ICP/MS	GL-MA-E-008	TAL and Specialty Metals	N/A	N
GEL	Acid Digestion of Sediments, Sludges, and Soils	GL-MA-E-009	TAL and Specialty Metals	N/A	N
GEL	Mercury Analysis using the Perkin-Elmer automated Mercury Analyzer	GL-MA-E-010	TAL Metals – Mercury	PE Hg Analyzer	N
GEL	Determination of Metals by ICP/MS with the Hewlett-Packard Model 4500 Spectrometer	GL-MA-E-014	TAL and Specialty Metals	ICP/MS	N
GEL	Colorimetric Determination of Chromium, Hexavalent	GL-GC-E-044	Hexavalent Chromium	Spectrophotometer	N
GEL	Sulfide	GL-GC-E-052	Sulfide	Spectrophotometer	N
GEL	Total Carbon and Total Organic Carbon Analysis using the Dohrmann DC-190 Boat Sampler	GL-GC-E-062	TOC	Dohrmann TOC Analyzer	N
GEL	Ion Chromatography (IC)	GL-GC-E-086	Sulfate,	IC	N

**TABLE 12.0.1
 FIXED LABORATORY ANALYTICAL METHOD/SOP REFERENCE**

Fixed Laboratory Performing Analysis	Standard Operating Procedure (SOP)	Code	Analytical Parameter	Instrument	Modified for Project Work Y or N
			Nitrite, Nitrate, Fluoride		
GEL	Hardness by Calculation	GL-GC-E-025	Hardness	N/A	N
GEL	Ferrous Iron (Phenanthrolin Method)	GL-GC-E-099	Ferrous Iron	N/A	N
GEL	Ferric Iron	(Calculation)	N/A	N/A	N/A
GEL	Isotopic Determination of Neptunium	GL-RAD-A-032	HTDR	Alpha Spec	N
GEL	Isotopic Determination of Plutonium-241	GL-RAD-A-035	HTDR	Alpha Spec	N
GEL	The Determination of Strontium 89/90 in Water, Soil, Milk, Meats, Fish, Vegetation, and Other Tissues	GL-RAD-A-004	HTDR	Gas Flow	N
GEL	The Determination of Technetium-99	GL-RAD-A-005	HTDR	Liquid Scintillation Counting	N
GEL	Determination of Americium, Curium, Plutonium, and Uranium	GL-RAD-A-011	HTDR	Alpha Spec	N
GEL	The Determination of Gamma Isotopes in Water and Soil	GL-RAD-A-013	Gamma	Gamma Spec	N
GEL	Determination of Thorium/Uranium	GL-RAD-A-038	Uranium and Thorium Isotopes	Alpha Spec	N
GEL	Digestion for Soil and Sand	GL-RAD-A-015	N/A	N/A	N

**TABLE 12.0.1
 FIXED LABORATORY ANALYTICAL METHOD/SOP REFERENCE**

Fixed Laboratory Performing Analysis	Standard Operating Procedure (SOP)	Code	Analytical Parameter	Instrument	Modified for Project Work Y or N
GEL	Soil Alkalinity using the EPA (Sobek) Method	EPA (Sobek) Method	Alkalinity	N/A	N
GEL	pH	GL-GC-E-008	pH	N/A	N
Southwest Research Institute	Determination Of Acid Volatile Sulfides And Simultaneously Extractable Metals In Sediment	TAP-01-0406-023	AVS:SEM	N/A	N
GE&E, LLC	Grain size	ASTM D422 – Method Followed (no SOP)	Grain size	N/A	N
Air Toxics, Inc.	Volatile Organics	Proprietary Information	Soil Gas Volatiles	N/A	N

SOPs are included in Appendix C.

Soil Alkalinity using the EPA (Sobek) Method

Principles

The amount of neutralizing bases, including carbonates, present in overburden materials is found by treating a sample with a known excess of standardized hydrochloric acid. The sample and acid are heated to insure that the reaction between the acid and the neutralizers goes to completion.

The calcium carbonate equivalent of the sample is obtained by determining the amount of unconsumed acid by titration with standardized sodium hydroxide.

Comments

A fizz rating of the neutralization potential is made for each sample to insure the addition of sufficient acid to react all the calcium carbonate present.

During digestion, do not boil samples. If boiling occurs, discard sample and rerun. Before titrating with acid, fill burette with acid and drain completely. Before titrating with base, fill burette with base and drain completely to assure that free titrant is being added to the sample.

Chemicals

1. Carbon dioxide-free water: Heat distilled water just to boiling in a beaker. Allow to cool slightly and pour into a container equipped with ascarite tube. Cool to room temperature before using.
2. Hydrochloric acid (HCl) solution, 0.1 N, certified grade (Fisher So-A-54 or equivalent).
3. Sodium hydroxide (NaOH), approximately 0.5 N: Dissolve 20.0 g of NaOH pellets in carbon dioxide-free water and dilute to 1 liter. Protect from CO₂ in the air with ascarite tube. Standardize solution by placing 50 ml of certified 0.1 N HCl in a beaker and titrating with the prepared 0.5 N NaOH until a pH of 7.00 is obtained. Calculate the Normality of the NaOH using the following equation:

$$N_2 = (N_1 V_1) / V_2, \text{ where}$$

V_1 = Volume of HCl used.

N_1 = Normality of HCl used.

V_2 = Volume of NaOH used.

N_2 = Calculated Normality of NaOH

4. Sodium hydroxide (NaOH) approximately 0.1 N: Dilute 200 ml of 0.5 N NaOH with carbon dioxide-free water to a volume of 1 liter. Protect from CO₂ in air with ascarite tube. Standardize solution by placing 20 ml of certified 0.1 N HCl in a beaker and titrating with the prepared 0.1 N NaOH until a pH of 7.00 is obtained. Calculate the Normality of the NaOH.
5. Hydrochloric acid (HCl), approximately 0.5 N: Dilute 42 ml of concentrated HCl to a volume of 1 liter with distilled water. Standardize solution by placing 20 ml of the known Normality NaOH prepared in a beaker and titrating with prepared HCl until a pH of 7.00 is obtained.

Calculate the Normality of the HCl using the following equation:

$$N_1 = (N_2V_2) / V_1, \text{ where}$$

V_2 = Volume of NaOH used.

N_2 = Normality of NaOH used.

V_1 = Volume of HCl used.

N_1 = Calculated Normality of HCl.

6. Hydrochloric acid (HCl), approximately 0.1 N: Dilute 200 ml of 0.5 N HCl to a volume of 1 liter with distilled water. Standardize solution as before, but use 20 ml of the known Normality NaOH
7. Hydrochloric acid (HCl), 1 part acid to 3 parts water: Dilute 250 ml of concentrated HCl with 750 ml of distilled water.

Materials

1. Flasks, Erlenmeyer, 250 ml
2. Burst, 100 ml (one required for each acid and one for each base).
3. Hot plate, steam bath can be substituted.
4. pH meter (Corning Model 12 or equivalent) equipped with combination electrode.
5. Balance, can be read to 0.01 g.

Procedure

1. Place approximately 0.5 g of sample (less than 60 mesh) on a piece of aluminum foil.
2. Add one or two drops of 1:3 HCl to the sample. The presence of CaCO_3 is indicated by a bubbling or audible "fizz."
3. Rate the bubbling or "fizz" in step 2 as indicated in Table 2.
4. Weigh 2.00 g of sample (less than 60 mesh) into a 250 ml Erlenmeyer flask.
5. Carefully add HCl indicated by Table 2 into the flask containing sample.
6. Heat nearly to boiling, swirling flask every 5 minutes, until reaction is complete. NOTE: reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask.

Table 2: Volume and Normality of Hydrochloric Acid Used for Each Fizz Rating (from [Sobek et al., 1978](#))

FIZZ RATING	HCl (ml)	HCl (NORMALITY)
None	20	0.1
Slight	40	0.1
Moderate	40	0.5
Strong	80	0.5

7. Add distilled water to make a total volume of 125 ml.

8. Boil contents of flask for one minute and cool to slightly above room temperature. Cover tightly and cool to room temperature. CAUTION: Do not place rubber stopper in hot flask as it may implode upon cooling.
9. Titrate using 0.1 N NaOH or 0.5 N NaOH (concentration exactly known), to pH 7.00 using an electrometric pH meter and burette. The concentration of NaOH used in the titration should correspond to the concentration of the HCl used in step 5. NOTE: Titrate with NaOH until a constant reading of pH 7.0 remains for at least 30 seconds.
10. If less than 3 ml of the NaOH is required to obtain a pH of 7.0, it is likely that the HCl added was not sufficient to neutralize all of the base present in the 2.00 g of sample. A duplicate sample should be run using the next higher volume or concentration of acid as indicated in Table 2.
11. Run a blank for each volume or normality using steps 5, 7, 8, and 9

Calculations

1. Constant (C) = (ml acid in blank) / (ml base in blank).
2. ml acid consumed = (ml acid added) - (ml base added x C).
3. Tons CaCO₃ equivalent / thousand tons of material = (ml of acid consumed) x (25.0) x (N of add).

Original Reference

Sobek, A., Schuller, Freeman, W.J. and Smith, R. (1978), *Field and Laboratory Methods Applicable to Overburdens and Minesoil*, (West Virginia Univ., Morgantown College of Agriculture and Forestry): EPA report no. EPA-600/2-78-054 p.47-50.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

**STANDARD OPERATING PROCEDURE
FOR
pH
(GL-GC-E-008 REVISION 9)**

APPLICABLE TO METHODS:
EPA 150.1, SW-846 Method 9040B,
SW-846 Method 9041A, SW-846 Method 9045C
Method 4500-H and Exhibit D Semivolatiles, OLMO4.2, 10.1.4.1

PROPRIETARY INFORMATION

This document contains proprietary information that is the exclusive property of General Engineering Laboratories, LLC (GEL). No contents of this document may be reproduced or otherwise used for the benefit of others except by express written permission of GEL.



TABLE OF CONTENTS

1.0	STANDARD OPERATING PROCEDURE FOR pH	3
2.0	METHOD CODE.....	3
3.0	METHOD OBJECTIVE/PURPOSE.....	3
4.0	METHOD SUMMARY.....	3
5.0	APPLICABLE MATRICES.....	3
6.0	HOLDING TIME.....	3
7.0	SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS.....	3
8.0	INTERFERENCES/LIMITATIONS.....	3
9.0	PERFORMANCE CHARACTERISTICS	4
10.0	DEFINITIONS.....	4
11.0	ANALYST VERIFICATION.....	4
12.0	DOCUMENTATION OF DATA	4
13.0	SAFETY PRECAUTIONS AND HAZARD WARNINGS	4
14.0	SAMPLE RECEIPT FOR ANALYSIS.....	5
15.0	INSTRUMENTATION/EQUIPMENT/GLASSWARE.....	5
16.0	REAGENTS	6
17.0	PREPARATION OF SAMPLES	6
18.0	PREPARATION OF STANDARDS.....	7
19.0	INSTRUMENT/EQUIPMENT START-UP PROCEDURES	7
20.0	QUALITY CONTROL (QC) REQUIREMENTS.....	8
21.0	RUN SEQUENCE.....	9
22.0	PROCEDURE.....	9
23.0	INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURES.....	11
24.0	DATA REVIEW, VALIDATION AND APPROVAL PROCEDURE(S).....	12
25.0	DATA TRANSMITTAL.....	12
26.0	RECORDS MANAGEMENT	12
27.0	ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE.....	12
28.0	LABORATORY WASTE HANDLING AND DISPOSAL.....	12
29.0	METHOD VERIFICATION	12
30.0	REFERENCES.....	12

1.0 STANDARD OPERATING PROCEDURE FOR PH**2.0 METHOD CODE**

- 2.1 Matrix - Water or multiphase waste where at least 20% of the sample is aqueous
 - 2.1.1 EPA 150.1
 - 2.1.2 Standard Methods 4500-H
 - 2.1.3 SW-846 Method 9040B
- 2.2 Matrix - Solids, Sludges, Oils
 - 2.2.1 SW-846 Method 9045C
- 2.3 Matrix - Liquid samples where measurement by the methods listed in 2.1 is not possible
 - 2.3.1 SW-846 Method 9041A (pH paper method) - This procedure is described in Section 22.1 of this SOP.

3.0 METHOD OBJECTIVE/PURPOSE

The purpose of this standard operating procedure (SOP) is to describe the procedures used to determine pH.

4.0 METHOD SUMMARY

- 4.1 For Methods EPA 150.1, Standard Methods 4500-H, SW-846 9040B, and SW-846 9045C: the pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.
- 4.2 For SW-846 Method 9041A: the pH is determined with pH paper. Skip directly to Section 22.1 for this procedure.

5.0 APPLICABLE MATRICES

- 5.1 Groundwater
- 5.2 Drinking water
- 5.3 Domestic and industrial wastewater
- 5.4 Soil
- 5.5 Sludge
- 5.6 Oil

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases the procedure is modified as necessary.

6.0 HOLDING TIME

pH samples are analyzed upon arrival unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

- 7.1 Samples can be collected in plastic or glass containers with no headspace.
- 7.2 Samples are unpreserved.
- 7.3 Samples are refrigerated at 4°C ±2° until the start of analysis in accordance with "Sample Receipt, Login, and Storage" (GL-SR-E-001).

8.0 INTERFERENCES/LIMITATIONS

- 8.1 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error electrode".

- 8.2 Oily material or particulate matter can coat the electrode and impair response. This is removed by gentle wiping and distilled water rinsing or by soaking in hydrochloric acid (1 + 9) if needed.
- 8.3 Temperature affects the pH of different samples in different ways. For this reason both pH and temperature should be recorded at time of analysis.
- 8.4 The Environmental Protection Agency (EPA) ruled on April 4, 1995, that the holding time for pH analysis is 15 minutes or less. Since transport of the samples to the laboratory for analysis exceeds this holding time, analysis occurs upon arrival.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method range: 0 to 14 pH units (s.u.)

9.2 Calibration range: 4 to 10 pH units (s.u.)

NOTE: Add a pH 2 buffer for acidic or a pH 12 buffer for caustic wastes when a sample is to be analyzed for corrosivity characterization.

9.3 Method precision: Refer to current SPC Limits

9.4 Method accuracy: Refer to current SPC Limits

10.0 DEFINITIONS

Buffer Solution - Solutions with known pH values that are used to perform daily calibrations of the pH meter.

Laboratory Control Sample (LCS) - Laboratory Control Standard (LCS) – An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and whether the laboratory is capable of making accurate and precise measurements.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

12.1 Sample preparation data is recorded in ALPHA LIMS.

12.2 As analytical data is obtained it is recorded in ALPHA LIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the laboratory.

13.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDSs are maintained in the laboratory.

13.3 Personal protective equipment

13.3.1 Approved gloves are required when handling chemicals or samples.

13.3.2 To prevent clothes and skin from being exposed to corrosive materials, wear a lab coat.

- 13.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:
- 13.4.1 Wear a dosimeter at all times while working in the lab to monitor radioactive exposure.
 - 13.4.2 Wear a plastic apron over lab coat when working with radioactive samples.
 - 13.4.3 Protect counter tops with counter paper or work from radioactive sample handling trays.
 - 13.4.4 Prohibit admittance to immediate work area.
 - 13.4.5 Post signs indicating radioactive samples are in the area.
 - 13.4.6 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.
 - 13.4.7 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.
- 13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.
- 13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.
 - 13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.
- 13.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts.
- 13.7 In the event of an accident or medical emergency call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.
- 13.8 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

14.0 SAMPLE RECEIPT FOR ANALYSIS

- 14.1 Login personnel are responsible for delivering samples for pH analysis to the pH work area in accordance with "Sample Receipt, Login, and Storage" (GL-SR-E-001).
- 14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

- 15.1 Orion Model EA 940 Expandable Ion Analyzer
- 15.2 Orion 81-04 or any other comparable combination pH electrode
- 15.3 Temperature compensation probe
- 15.4 Beakers (minimum capacity needed - 25 mL)
- 15.5 Magnetic stir plate
- 15.6 Stirrer magnets
- 15.7 If Method 9045C is being used:
 - 15.7.1 Centrifuge
 - 15.7.2 Centrifuge tubes (minimum capacity - 50 mL)

- 15.7.3 Top-loader balance
- 15.7.4 Spatula
- 15.7.5 Separatory funnel (optional)
- 15.8 If Method 9041A is being used:
 - 15.8.1 pH paper

16.0 REAGENTS

- 16.1 pH 4 Calibrating Buffer (Preferred brand: Baxter S/P)
- 16.2 pH 7 Calibrating Buffer (Two sources are required. The preferred brand for calibration is Baxter S/P. A second source is needed for a Laboratory Control Sample (LCS)).

NOTE: If the client specifies, a pH 2 buffer will be run as the LCS for a corrosivity batch containing acidic samples. For a corrosivity batch containing caustic samples, a pH 12 buffer will be run.

- 16.3 pH 10 Calibrating Buffer (Preferred brand: Baxter S/P)
- 16.4 ASTM Type II Deionized (DI) water

17.0 PREPARATION OF SAMPLES

- 17.1 Sample preparation for soils, sludges, oils, miscellaneous solids, and liquids where less than 20% of the sample is aqueous:

NOTE: No sample preparation is required when more than 20% of the sample is aqueous.

- 17.1.1 A beaker is placed on the top-loader balance. Tare the balance.
- 17.1.2 A minimum of 20 g of sample is placed in the beaker. The sample aliquot is mixed as thoroughly as possible and is representative of the sample.
- 17.1.3 A volume in milliliters of deionized water equal to the weight in grams of the sample aliquot is measured in a graduated cylinder.

NOTE: If the sample is hygroscopic and absorbs all the reagent water begin the prep again using a mass of water equal to two times the mass of sample.
- 17.1.4 The water is placed in the beaker with the sample aliquot.
- 17.1.5 Stir the water and sample aliquot continuously for five minutes.
- 17.1.6 After five minutes the mixture is allowed to stand for one hour so any suspended matter can settle. If time is limited, the sample can be centrifuged.

NOTE: If the sample is a waste material, allow the sample to stand for only 15 minutes.

- 17.1.7 After the majority of the suspended matter has settled out, the water layer is decanted off into a separate beaker.

NOTE: When preparing oils for analysis it may be necessary to use a separatory funnel to separate the water layer after extraction. Only the aqueous phase of the supernatant is to be analyzed.

- 17.1.8 Transfer 50 g soil/sediment to a 100 mL beaker. Add 50 mL of water and stir for 1 hour. Determine pH of sample with a pH meter while stirring.
- NOTE:** If limited sample volume is received, use smaller 1:1 ration of grams of soil/sediment sample to mLs of water for the pH determination.
- 17.1.9 The pH of the decanted liquid is obtained using the combination pH electrode as described in Section 22.0.

18.0 PREPARATION OF STANDARDS

- 18.1 Documentation of standards is maintained in accordance with "Laboratory Standards Documentation" (GL-LB-E-007).
- 18.2 Laboratory Control Sample(s): Commercially available pH buffer of 7.00 ±0.01 @ 25°C. This must be from a different source than the calibrating pH 7 buffer.
- 18.3 Calibration standards:
- 18.3.1 pH buffers: 4, 7, and 10 pH units.
- NOTE:** If a sample is being analyzed for corrosivity, the pH meter calibration must also include buffers of pH 2 and pH 12.
- 18.3.2 The buffers for calibration are stored in the wet chemistry area in the cabinets near the pH meter.
- 18.3.3 Buffers are discarded when they exceed the manufacturer's expiration date.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURES

- 19.1 The combination pH electrode must be plugged into either the #1 or #2 sensing electrode jack on the rear part of the meter. The temperature compensating electrode is plugged into the ATC jack. A diagram for this is shown on page 4 of the Model EA 940 Instruction Manual.
- 19.2 If the meter is already set up and the electrodes are in place, the screen should read either "1:pH" or "2:F-". To switch from the F- electrode to pH, press "**2nd function**", "2". Once the pH electrode is selected go to section 19.4.
- 19.3 If the meter was unplugged or is being reprogrammed, the screen should read "Operator Menu". Press "yes".
- 19.4 The screen should now read "Change the electrode ID?" Press "yes".
- 19.5 The screen should now list four different choices. Press the number that corresponds to pH.
- 19.6 The screen should read "pH ISO = 7.000". If not enter this number. Once the number is shown, press "yes".
- 19.7 The screen should now read "Set number of decimal places?" Press "yes", then press "2" for the decimal places.
- 19.8 The screen should now read "Change the pH limits?" Press "yes" to see what limits are set.
- 19.9 The screen should now display "pH high limit = 19.99 OK?" If not enter this number, then press "yes".

- 19.10 The screen should now read "pH low limit = -2.00 OK?" If not enter this number, then press **"yes"**.
- 19.11 The screen should now read "Change the print interval?" Since the meter is not currently connected to a printer, press **"no"**.
- 19.12 The screen should now read "Set the timer?" Press **"no"**.
- 19.13 The screen should now read "Set temperature?" Since an ATC (Automatic Temperature Compensating) electrode will be used, press **"no"**.
- 19.14 The screen should now read "Change the time and date?" Press **"yes"**. The screen should now give a readout of time in hours-minutes-seconds. If the numbers shown are not correct, the proper values are entered. Once the proper values are shown, press **"yes"**.
- 19.15 The screen should now show the correct date in month-day-year. If this is not correct, the proper values are entered. Once the proper values are shown, press **"yes"**.
- 19.16 The screen should now read "Enter standby mode?" Press **"no"**.
- 19.17 The screen should now read "Operator Menu?" Because all the parameters for performing pH analysis have been entered, press **"no"**.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

- 20.1 The pH calibration must be checked by measuring the pH of all buffers used to calibrate the meter. The pH must be within 0.05 pH units of the buffer solution value. If they are not, the calibration must be repeated until this criteria is met.
- 20.2 Frequency of QC:
- 20.2.1 A matrix duplicate is run for every group of ≤ 10 samples and for each set of ten samples in batches with > 10 samples.
- 20.2.2 A laboratory control sample is run once per batch unless specified otherwise by the client.
- 20.2.3 An initial calibration verification (ICV) is run immediately after the calibration. A continuing calibration verification (CCV) is run after every 10 samples and after the last sample in the run.
- 20.3 Acceptance limits:
- 20.3.1 Matrix relative percent difference (RPD): See current SPC limits
- 20.3.2 LCS: See current SPC limits or client specified limits, whichever are more stringent.
- 20.3.3 ICV and CCV must be ± 0.05 s.u.
- 20.4 Handling out-of-control situations:
- 20.4.1 All QC data is calculated as soon as the results for the QC samples are known.
- 20.4.1.1 If the Matrix RPD falls outside of the SPC limits, reanalyze that sample.
- 20.4.1.2 If the LCS RPD, or LCS Recovery falls outside of the SPC limits, the pH meter is to be recalibrated and all samples bracketed by the LCS and LCS DUP must be reanalyzed.

21.0 RUN SEQUENCE

- 21.1 Calibration standards: pH 4, 7 and 10 buffer solutions
- 21.2 pH 7 LCS (2nd Source Standard)
- 21.3 CCV (Continuing Calibration Verification)
- 21.4 Samples 1 through x where $x \leq 10$
- 21.5 Sample x duplicate
- 21.6 Repeat steps 21.3 - 21.5 for every group of 10 samples in the batch. Run an additional CCV after the last analytical sample in the run.

22.0 PROCEDURE

- 22.1 Sample Analysis by SW-846 Method 9041A - "pH Paper Method" - for solvents and other samples that could possibly damage the electrodes, paper pH strips may be used to determine pH.

NOTE: This method is not considered to be as accurate for pH measurement as pH meters; for this reason, pH measurements taken by Method 9041A cannot be used to define a waste as alkaline and non-corrosive.

NOTE: If a sample masks color changes on the pH paper, this method is not reliable.

- 22.1.1 Place a pH strip into a small aliquot of sample.
- 22.1.2 The color change of the pH strip is compared to the color patterns listed on the pH strip box.
- 22.1.3 Record the pH in AlphaLIMS.

NOTE: Each batch of pH paper must be calibrated (checked) against certified pH buffers. The paper must read within 0.5 pH units of the certified pH of the buffer. This calibration is recorded in the pH calibration log.

- 22.1.4 Analyze each sample in duplicate by repeating Steps 22.1.1 - 22.1.3.
- 22.1.5 Using a thermometer calibrated in accordance with "Thermometer Calibration" (GL-QS-E-007), measure the temperature of one of the sample aliquots used during narrow-range pH analysis. This is the temperature of the sample at the time the pH was measured.
- 22.1.6 Record the temperature of the sample in AlphaLIMS.
- 22.2 Calibration for methods using a pH meter:
 - 22.2.1 Before the meter is calibrated, the combination pH electrode is checked to make sure it is filled with Orion No. 810007 Internal Filling Solution. No filling solutions containing silver are used.
 - 22.2.2 After having gone through the startup procedure, the meter should read "Operator Menu" as described in 19.17. Press "**no**".
 - 22.2.3 The meter should now read "Calibrate pH?" Press "**yes**".
 - 22.2.4 The screen should now read "Enter number of buffers (1-3)". Press "**3**".
 - 22.2.5 The screen should now read "Do automatic pH calibration?" Press "**no**".
 - 22.2.6 The screen should now read "pH electrode placed in buffer 1?" At this time a fresh beaker of pH 4 buffer is poured. A small stirring magnet is

- rinsed and placed in the beaker. The beaker is placed on top of the magnetic stirrer and the stir control is adjusted to maintain a slow, steady rate of stirring.
- 22.2.7 The combination pH electrode and the temperature compensating electrode are rinsed thoroughly with deionized water and lowered into the beaker. Press **"yes"**.
- 22.2.8 Once the reading has stabilized, the meter will read "Calibrate as 4.00" or whatever the correct value for the 4 buffer should be given the temperature of the buffer. The value reading for the buffer should be very close to this reading. Press **"yes"**.
- 22.2.9 The electrodes are removed from the beaker and rinsed. A fresh aliquot of pH 7 buffer is poured into a clean beaker. This beaker is placed on top of the stirrer and a clean stirring magnet is placed in it.
- 22.2.10 The meter should now read "pH electrode placed in buffer 2?" The electrodes are placed in the buffer. Press **"yes"**.
- 22.2.11 Once the reading has stabilized, the meter will read **"Calibrate as 7.00"**. The value reading for the buffer should be very close to this reading. Press **"yes"**.
- 22.2.12 The electrodes are removed from the beaker and rinsed. A fresh aliquot of pH 10 buffer is poured into a clean beaker. The beaker is placed on top of the stir plate and a clean stirring magnet is placed in it.
- 22.2.13 The meter should now read **"pH electrode placed in buffer 3?"**. The electrodes are placed in the buffer. Press **"yes"**.
- 22.2.14 Once the reading has stabilized, the meter will read **"Calibrate to 10.00"**. The value reading for the buffer reading should be very close to this reading. Press **"yes"**.
- 22.2.15 The meter is now calibrated. Re-analyze all 3 buffers. The buffers should read ± 0.05 pH units of their true values. If not, recalibrate.
- 22.2.16 If there are no samples to be run immediately after the meter calibration is completed, the electrode is left soaking in pH 7 buffer.
- 22.3 Sample Analysis by methods using a pH meter:
- 22.3.1 When the slope has been displayed, the meter should also read "Yes to continue?" Press **"yes"**.
- 22.3.2 The meter should now read "Measure pH?" Press **"yes"**. The meter should show a pH value, current time and the current temperature. In addition, when the meter reading has stabilized "Ready" will appear between the time and temperature. This indicates that the millivolts have stabilized enough to give an accurate value.
- 22.3.3 Shake each sample prior to analysis. Approximately 40 mL of sample is poured into a beaker.
- NOTE:** If the sample was prepared as described in 17.1, the decanted layer is the sample aliquot.

- 22.3.4 Place the beaker containing the sample on a magnetic stirring plate and drop a clean stirring bar into the sample aliquot.
- 22.3.5 Adjust the stir control to maintain a slow, steady rate of stirring.
- 22.3.6 Lower the pH electrode and the temperature compensating probe into the beaker.
- 22.3.7 When the "Ready" status is displayed for each sample, record the pH of the sample, temperature and time the reading was taken in the appropriate columns of the pH data entry screen in AlphaLIMS.
- 22.3.8 Repeat steps 22.3.3 through 22.3.7 with successive sample aliquots until the pH values obtained differ by < 0.1 pH units.
- 22.3.9 Run the samples in the sequence described in Section 21.0
- NOTE:** If only a few samples are ready to be run at a time, a duplicate sample is run for each set, regardless of whether or not ten samples have been run since the last set of QC. The reason for this is to prove electrode repeatability throughout the day.
- 22.3.10 After all the pH samples present have been analyzed, the pH electrode is placed back in the pH 7 buffer.
- 22.4 Calculation/reporting of results:
- 22.4.1 Each sample result has a corresponding temperature and run time. These are recorded in ALPHA LIMS. The final pH reading obtained for a sample after the criteria in 22.2.8 has been met is the one that is reported.
- 22.4.2 When submitting data for data entry, record the analyst's name, date of analysis, time, temperature, and pH values in ALPHA LIMS.
- 22.4.3 After every duplicate sample value is recorded, the RPD (relative percent difference) of the sample and the duplicate are calculated. This is done by subtracting the lower value from the higher value, dividing by the average of the two and multiplying by 100 as shown in this formula:
- $$\frac{\text{High value} - \text{Low value}}{\text{Average of the two values}} \times 100 = \text{RPD}$$
- 22.4.4 If the RPD is within the current control limits for pH, the duplicate is acceptable.
- 22.4.5 If the RPD is greater than the control limit, the sample and the duplicate are rerun. If the RPD is outside of the acceptance limits after being rerun, the pH meter is recalibrated and all samples analyzed prior to this duplicate and after the last acceptable duplicate are reanalyzed.
- 22.4.6 LCS RPDs are calculated using the formula described in 22.4.3.
- 22.4.7 LCS recoveries are calculated using this formula:
- $$\frac{\text{actual value obtained}}{\text{theoretical value}} \times 100 = \% \text{ LCS recovery}$$

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURES

- 23.1 After all the samples have been run, both the pH electrode and temperature compensating probe are rinsed thoroughly with DI water.

23.2 The electrode and probe are placed in a beaker filled with pH 7 buffer.

24.0 DATA REVIEW, VALIDATION AND APPROVAL PROCEDURE

Refer to GL-LB-E-005 and GL-GC-E-092 for data review and validation procedures.

25.0 DATA TRANSMITTAL

When a batch is given General Chemistry departmental "DONE" status, the data becomes available to reporting personnel.

26.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

27.1 The combination pH electrode is drained and refilled with the appropriate filling solution as needed.

27.2 For problems that occur during operation, refer to the troubleshooting checklists located in the Orion Ross pH Electrode Instruction Manual or the Orion Model EA 940 Expandable Ion Analyzer Instruction Manual.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

The pH test paper method SW-846 9041A is used only for miscellaneous samples. For safety reasons, the interference screening procedure described in section 17.3 of SW-846 9041A has not been included in this SOP.

30.0 REFERENCES

- 30.1 Method for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Method 150.1, "pH, Electrometric".
- 30.2 Orion Model EA 940 Expandable Ion Analyzer Instruction Manual
- 30.3 Orion Ross pH Electrode Instruction Manual
- 30.4 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1C, SW-846, 3rd Edition, June 1997. USEPA Office of Solid Waste and Emergency Response, Washington, DC. 20460:
 - 30.4.1 Method 9045C, "Soil and Waste pH," Revision 3, January 1995.
 - 30.4.2 Method 9040B, "pH Electrometric Measurement," Revision 2, January 1995.
 - 30.4.3 Method 9041A, "pH Paper Method," Revision 1, July 1992.
- 30.5 Standard Methods, 18th edition, Method 4500-H, "Electrometric Measurement."
- 30.6 Exhibit D, Semivolatiles, Section 10.1.4.1, OLMO4.2

DETERMINATION OF ACID VOLATILE SULFIDES AND SIMULTANEOUSLY EXTRACTABLE METALS IN SEDIMENT

1.0 SCOPE

- 1.1 This method describes procedures for the determination of acid volatile sulfides (AVS) and for metals that are solubilized during the acidification step (simultaneously extracted metal, SEM).
- 1.2 The conditions used have been reported to measure amorphous or moderately crystalline monosulfides:
 - 1.2.1 As a precipitant of toxic heavy metals, sulfide is important in controlling the bioavailability of metals in anoxic sediments.
 - 1.2.2 If the molar ratio of toxic metals measured by SEM to AVS exceeds one, the metals are potentially bioavailable.
- 1.3 Because the relative amounts of AVS and SEM are important in the prediction of potential metal bioavailability, it is important to use the SEM procedure for sample preparation for metals analysis. This uses the same conditions for release of both sulfide and metal from the sediment and thus provides the most predictive means of assessing the amount of metal associated with sulfide.

2.0 RESPONSIBILITIES

- 2.1 It is the responsibility of the Project Manager/Lab Supervisor to assure that all steps described in this procedure are performed.
- 2.2 It is the responsibility of the laboratory personnel to comply with all the steps in this procedure.

3.0 SUMMARY

- 3.1 The AVS in the sample is first converted to hydrogen sulfide (H₂S) by acidification with hydrochloric acid at room temperature. The H₂S is then purged from the sample and trapped. The amount of sulfide that has been trapped is then determined. The SEM are metals liberated from the sediment during the acidification. These are determined after filtration of the sample.

- 3.2 Two types of apparatus for sample purging and trapping of H₂S are described. One uses a series of Erlenmeyer flasks while the other uses flasks and traps with ground glass stoppers. The former is less costly. The latter is less prone to leakage that causes low recovery of AVS. The latter is recommended when higher degrees of precision are desired and for samples containing low levels of AVS.
- 3.3 Three means of quantifying the H₂S released by acidifying the sample are provided. In the gravimetric procedure, the H₂S is trapped in silver nitrate. The silver sulfide that is formed is determined by weighing. This procedure is recommended for samples with moderate or high AVS concentrations. In the colorimetric method, the H₂S is trapped in sodium hydroxide. The sulfide is converted to methylene blue that is measured. This procedure is recommended for samples that have low to moderate AVS concentrations. In an alternative procedure the H₂S is trapped in an antioxidant buffer before using an ion-selective electrode.
- 3.4 After release of the H₂S, the acidified sediment sample is membrane filtered before determination of the SEM by atomic absorption or inductive coupled plasma spectrometric methods.

4.0 DEFINITIONS

- 4.1 ACID VOLATILE SULFIDES (AVS) - Amorphous, moderately crystalline monosulfides, and other sulfides that form hydrogen sulfide under the conditions of this test.
- 4.2 SIMULTANEOUSLY EXTRACTED METALS (SEM) - Metals commonly cadmium, copper, lead, mercury, nickel and zinc, which form less soluble sulfides than do iron or manganese, and which are at least partially soluble under the conditions of this test.
- 4.3 METHOD DETECTION LIMIT (MDL) - The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from the analysis of a sample that contains the analyte with a given matrix.
- 4.4 LABORATORY REAGENT BLANK (LRB) - An aliquot of reagent water or reagents that is treated exactly as a sample including exposure to all glassware, equipment, and reagents that are used with samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.

- 4.5 STOCK STANDARD SOLUTION - A concentrated solution of the analyte prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source.
- 4.6 CALIBRATION STANDARDS (CAL) - Solutions prepared from the stock standard solution that is used to calibrate the method response with respect to analyte concentration.
- 4.7 LABORATORY FORTIFIED BLANK (LFB) - An aliquot of reagent water or reagents to which a known quantity of the method analyte is added in the laboratory. The LFB is analyzed exactly like a sample. Its purpose is to determine whether the method is within accepted control limits.
- 4.8 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) - An environmental sample to which a known quantity of the method analyte is added in the laboratory. The LFM is analyzed exactly like a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytical results.

5.0 INTERFERENCES

- 5.1 Oxygen in the reagents and apparatus is the primary interference reported. Special precautions must be taken to insure that the analytical system is adequately purged with oxygen-free nitrogen. Argon may be substituted for nitrogen if it is important that an even lower level oxygen concentration be maintained.
- 5.2 The pH of the sample after the addition of the acid and during the purge process must be below 3. Typically, the pH is below 2.

6.0 SAFETY

- 6.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical and environmental sample should be regarded as a potential health hazard and exposure should be minimized. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should be available to all personnel involved in the chemical analysis.

- 6.2 Hydrogen sulfide is a highly poisonous, gaseous compound having a characteristic odor of rotten eggs. It is detectable in air by humans at a concentration of approximately 0.002 ppm. Handling of acid samples should be performed in a hood or well ventilated area. If hydrogen sulfide is detected in the air by the laboratory staff, sample handling procedures must be corrected.

7.0 MATERIALS - APPARATUS AND EQUIPMENT

7.1 Glassware

- 7.1.1 AVS evolution and H₂S trapping - Glassware that provides a high precision of accuracy for samples is recommended..

7.1.1.1 For highest precision and low AVS levels - For each analytical train 500 mL gas washing bottles, one 250 mL round bottom flask with a septum (Ace Glass 6934 or equivalent), 100 or 250 mL impingers. The round bottom flask contains the sediment and acid is introduced to it by a syringe inserted through the septum. The flasks are connected by plastic tubing. In all cases the inlets are below the liquid level and the outlets are above the liquid levels. The apparatus is assembled and more than one analytical train can be connected to a single cylinder of nitrogen if flow controllers are installed in the line. Different amounts of glassware are required for each of the three means of sulfide determination.

7.1.1.2 For routine analysis - Erlenmeyer flasks, 250 mL, are substituted for the gas washing bottle, the round bottom flask and the impingers. The flask size should be consistent with sample size and reagent volumes. A thistle tube fitted with a stopcock or a separatory funnel is provided to introduce acid to the flask containing the sediment sample. This flask is fitted with a three hole stopper. One hole is for the thistle tube or separatory funnel and the other two are for the gas inlet and outlet. The other flasks are fitted with two hole stoppers; one hole is for the gas inlet and the other is for the gas outlet. The gas inlets are below the liquid level and the gas outlets are above the liquid level. The flasks are connected by plastic tubing.

- 7.1.2 Evaporating dishes, porcelain, 100 mL.
- 7.1.3 Assorted calibrated pipettes and volumetric flasks.
- 7.2 Drying oven - Capable of maintaining a constant temperature in the range of 100 - 104E C.
- 7.3 Analytical balance - of weighing to 0.0001 g.
- 7.4 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.
- 7.5 Gravimetric method
 - 7.5.1 Filtering flask.
 - 7.5.2 Filter holder for 47 mm filter.
- 7.6 Colorimetric method
 - 7.6.1 Spectrophotometer - Capable of measuring absorbance at 670 nm.
 - 7.6.2 Spectrophotometer cells.
- 7.7 Ion-selective electrode method
 - 7.7.1 Electrometer, pH meter or ion-selective meter - Compatible with the use of ion-selective electrodes.
 - 7.7.2 Sulfide selective electrode.
- 7.8 Atomic absorption or inductive couple plasma spectrophotometer for the determination of SEM.

8.0 MATERIALS - REAGENTS AND CONSUMABLE MATERIALS

- 8.1 All water and reagents used in this method must be free of dissolved oxygen and sulfides. Freshly prepare and use deaerated, deionized water, DDIW, by purging dissolved oxygen from the deionized water by vigorously bubbling with oxygen free nitrogen approximately one hour. Deaerate reagents by purging with nitrogen.
- 8.2 Sodium sulfide standard - Required for quality assurance and calibration.

8.2.1 Sulfide stock standard solution, approximately 0.05M or 50 $\mu\text{moles/mL}$.

8.2.1.1 Place a few crystals of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in a beaker. Wash them with distilled water and dry them by blotting with filter paper. Weigh about 12 gram of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and dissolve it in 1,000 mL of DDIW. Store in a brown bottle.

8.2.1.2 Standardize against thiosulfate solution.

8.2.1.2.1 Pipette 10.00 mL of 0.025N standard iodine solution (Section 9.2.2) into each of two 125-mL Erlenmeyer flasks.

8.2.1.2.2 Pipette 2.00 mL of sulfide stock standard solution into one flask. Pipette 2.00 mL of DDIW, as a laboratory reagent blank, into the other flask.

8.2.1.2.3 Add 5.00 mL of 6M HCl into each flask, swirl slightly, then cover and place in the dark for 5 minutes.

8.2.1.2.4 Titrate each with 0.025 N thiosulfate (Section 9.2.3), adding soluble starch indicator when the yellow iodine color fades. The end point is reached when the blue color disappears.

8.2.1.2.5 Calculate the sulfide concentration as follows:

$$\text{Sulfide, } (\mu\text{mol} / \text{mL}) = \frac{(T_{\text{blank}} - T_{\text{sample}}) \times N S_2O_3^{2-}}{(V_{\text{sample}}) \times 2 \text{ equiv } S^{2-}} \times \frac{1 \text{ mole } S^{2-}}{1 \text{ mmole}} \times 1000 \mu\text{moles}$$

where

T = volume of titrant used for the blank and sample (mL)

N = concentration of $\text{S}_2\text{O}_3^{2-}$ titrant

V = Volume of sample used (2.00 mL)

8.2.2 Standard iodine solution, 0.025N - Dissolve 20 to 25 gram potassium iodide, KI, in a small volume of deionized water, add 3.2 gram iodine, and dilute to 1,000mL. Standardize against 0.025N sodium thiosulfate (Section 8.2.3) using starch solution as indicator.

8.2.3 Standard sodium thiosulfate solution, 0.025N. May be purchased commercially or prepared in the laboratory. If prepared in the laboratory, it should be standardized against potassium dichromate.

8.2.3.1 Weigh approximately 6.2 g of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ into a 500 mL beaker. Add 0.1 g sodium carbonate, Na_2CO_3 , and dissolve in 400 mL deionized water. Pour into a 1.0 L volumetric flask and dilute to volume with deionized water.

8.2.3.2 Standardize against potassium dichromate, K_2CrO_7

8.2.3.2.1 Accurately weigh approximately 0.2 g dry K_2CrO_7 and place in a 500 mL Erlenmeyer flask. Dissolve in 50 mL deionized water.

8.2.3.2.2 Dissolve 3 g of potassium iodide, KI, in 50 mL distilled water, add 5 mL of 6M HCl and add to K_2CrO_7 solution. Swirl, cover and store in the dark for 5 minutes. Add 200 mL deionized water and titrate with the thiosulfate solution, adding starch indicator when the yellow iodine color fades, until the blue color turns to pale green.

8.2.3.2.3 Calculate the thiosulfate concentration as follows:

$$N(\text{S}_2\text{O}_3^{2-}) = \frac{\text{g } \text{K}_2\text{CrO}_7}{\text{mL } \text{S}_2\text{O}_3^{2-}} \times \frac{1 \text{ mole } \text{K}_2\text{CrO}_7}{294.19 \text{ g } \text{K}_2\text{CrO}_7} \times \frac{6 \text{ equiv } \text{K}_2\text{CrO}_7}{1 \text{ mole } \text{K}_2\text{CrO}_7} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

8.2.4 Starch indicator - Dissolve 1.0 gram soluble starch in 100 mL boiling deionized water.

8.2.5 Sulfide working standards - Prepare sulfide working standards using the sulfide stock standard solution in Section 9.2.1. The concentrations of the following standards will depend on the exact concentration of the sulfide stock standard determined in Section 9.2.1.2.5. Correct concentrations of the standards in the following part of this section and the amount of sulfide in standards used in the colorimetric method in Section 14.2.5 by multiplying by a factor of the concentration determined in Section 9.2.1.2.5 divided by 50 umoles/mL.

8.2.5.1 Prepare sulfide working standard A by diluting 1.00 mL of sulfide stock standard to 100.0 mL. This solution contains 0.5 umole sulfide/mL, if the concentration of the sulfide stock standard is exactly 0.05 M.

8.2.5.2 Prepare sulfide working standard B by diluting 10.00 mL of sulfide stock standard to 100.0 mL. This solution contains 0.5 umole sulfide/mL, if the concentration of the sulfide stock standard is exactly 0.05 M.

8.3 AVS evolution

8.3.1 Hydrochloric acid 6M - Dilute 500 mL of concentrated hydrochloric acid (sp. gr. 1.19) to 1L with deionized water.

8.3.2 Nitrogen gas, oxygen free, with regulator and flow controller. An oxygen gas scrubber may be required and is available commercially or deoxygenating solutions may be placed in the flask or gas washing bottle placed first in the analytical train.

8.3.3 Plastic hypodermic syringe, 30 mL, and needle.

9.0 PROCEDURES

9.1 Gravimetric method

9.1.1 Potassium acid phthalate, 0.05M - Dissolve 10.2 g of potassium acid phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$, in DDIW and dilute to 1L.

9.1.2 Silver nitrate, 1M - Dissolve 17 g of silver nitrate, AgNO_3 in DDIW and dilute to 1 L. Store in a dark bottle.

9.1.3 Glass fiber filters, 1.2 micron - Predry filters at 102E C.

9.2 Colorimetric method

9.2.1 Sodium hydroxide solution, 1M - Dissolve 40 g sodium hydroxide in 1000 mL DDIW.

9.2.2 Sodium hydroxide solution, 0.5M - Dissolve 20 g sodium hydroxide in 1000 mL DDIW.

9.2.3 Mixed diamine reagent, MDR

9.2.3.1 Component A - Add 660 mL concentrated sulfuric acid to 340 mL of DDIW. After the solution cools, dissolve 2.25 g N-N-dimethyl-p-phenylenediamine oxalate in it.

9.2.3.2 Component B - Dissolve 5.4 g ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$) in 100 mL concentrated hydrochloric acid and dilute to 200 mL with DDIW.

9.2.3.3 Mixed diamine reagent, MDR - Mix components A and B.

9.2.4 Sulfuric acid solution, 1.0M - Dilute 56 mL concentrated sulfuric acid (H_2SO_4) to 1 L with DDIW.

9.3 Ion-selective electrode method

9.3.1 Sodium hydroxide solution - Dissolve 80 g of sodium hydroxide in 700 mL of DDIW with caution. Cool to room temperature.

9.3.2 Sulfide anti-oxidant buffer (SAOB) - To the sodium hydroxide solution in Section 7.6.1 add and dissolve 74.45 g of disodium ethylenediaminetetraacetic acid and 35.23 g of ascorbic acid. Dilute to 1 L with DDIW.

10.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

10.1 Sulfide ion is unstable in the presence of oxygen. Protect sediment samples from exposure to oxygen during sample collection and storage.

10.2 During storage sulfides can be formed or lost due to biological activity and sulfide can be lost by volatilization or oxidation. Metal speciation can change as a result of changes in sulfide concentration and as a result of other changes in the sample.

10.3 Samples should be collected in wide mouth jars with a minimum of air space above the sediment. If possible, the headspace should be purged with oxygen free nitrogen. The jars must have Teflon or polyethylene liners.

- 10.4 Samples should be cooled to 4° C as soon as possible after collection. Samples maintained at 4° C have been found to have no significant loss of AVS for storage periods up to 2 weeks. Anoxic sediments stored at 4° C for 20 days show significant changes in metal partitioning, suggestive of oxidation of the sediment. Holding time for samples should not exceed 14 days.

11.0 CALIBRATION AND STANDARDIZATION

- 11.1 Calibrate the photometer with a minimum of four standards and a blank that cover the expected range of the samples. Prepare a calibration graph relating absorbance to the μ moles of sulfide taken.
- 11.2 Calibrate the sulfide electrode system with a minimum of three standards that cover the expected range of the samples. Standards must be made up in SAOB diluted 1+1 with DDIW. Follow the manufacturer's instructions for use of the electrode.
- 11.3 Overall sulfide recovery is determined by analysis of a known amount of sodium sulfide standard added to DDIW from which the sulfide is liberated in the analysis train (LFB). Recoveries of 95% \pm 10% are expected.

12.0 ACCEPTANCE CRITERIA - QUALITY CONTROL

- 12.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirement of this program consists of an initial demonstration of laboratory capability, and the analysis of laboratory reagent blanks, fortified blanks and samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data thus generated.
- 12.2 INITIAL DEMONSTRATION OF PERFORMANCE
- 12.2.1 The initial demonstration of performance is used to characterize instrument performance, method detection limits, and linear calibration ranges.

12.2.2 Method detection limit (MDL) - The method detection limit should be established for the analyte, using DDIW (blank) fortified at a concentration two to five times the estimated detection limit (10). To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$\text{MDL} = t \times s$$

where

t = students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates)
s = standard deviation of the replicate analyses

Method detection limits should be determined every six months or whenever a significant change in background or instrument response is expected.

12.2.3 Linear calibration ranges - The upper limit of the linear calibration range should be established by determining the signal responses from a minimum of four different concentration standards covering the expected range, one of which is close to the upper limit. The linear calibration range that may be used for the analysis of samples should be judged by the analyst from resulting data. Linear calibration ranges should be determined every six months or whenever a significant change in instrument response may be expected.

12.3 ASSESSING LABORATORY PERFORMANCE - REAGENT AND FORTIFIED BLANKS

12.3.1 Laboratory reagent blank (LRB) - The laboratory must analyze at least one reagent blank (3.4) with each set of samples. Reagent blank data are used to assess contamination from the laboratory environment and reagents. If an analyte value in the reagent blank exceeds its determined MDL, then laboratory or reagent contamination should be suspected. Any determined source of contamination should be corrected and the samples reanalyzed.

12.3.2 Laboratory fortified blank (LFB) - The laboratory must analyze at least one fortified blank (3.7) with each batch of samples. Calculate accuracy as percent recovery. If the recovery of the analyte falls outside the control limits (see 10.3.3), the analyte is judged to be out of control, and the source of the problem should be identified and resolved before continuing analyses.

12.3.3 Until sufficient data become available from within their own laboratory (usually a minimum of twenty to thirty analyses), the laboratory should assess laboratory performance against recovery limits of 85 - 105%. When sufficient internal performance data becomes available, develop control limits from the mean recovery (\bar{x}) and the standard deviation (s) of the mean recovery. These data are used to establish upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \bar{x} + 3s$$

$$\text{LOWER CONTROL LIMIT} = \bar{x} - 3s$$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent twenty to thirty data points.

12.4 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIES SAMPLE MATRIX

12.4.1 The laboratory must fortify a minimum of 10% of the routine samples or one fortified sample per set, whichever is greater. Ideally, the concentration should at least double the background concentration. Overtime, samples from all routine sample sources should be fortified.

12.4.2 Calculate the percent recovery for the analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the control limits established in Section 10.3.3 for the analyses of LFBs. Spike recovery calculations are not required if the spike concentration is less than 10% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = (C_s - C_b) / S \times 100$$

where

R = percent recovery,
C_s = fortified sample concentration,
C_b = sample background concentration, and
S = concentration equivalent of the fortified sample.

12.4.3 If the recovery of the analyte in the fortified sample falls outside the designated range, and the laboratory performance on the LFB for the analyte is shown to be in control (Section 10.3) the recovery problem encountered with the fortified sample is judged to be matrix related, not system related.

13.0 GENERATION OF H₂S

13.1 Assemble glassware according to the detection method to be used. The setup should be followed as a general guide. In all cases a flask or gas washing bottle containing a deoxygenating solution may be placed in the sample train between the nitrogen tank and the first flask. It is recommended that nitrogen be controlled by a flow-controller, but an equivalent flow rate may be regulated by a clamp and bubble rate determined. In all cases the glassware will minimally consist of a H₂S generating flask and a series of traps.

13.1.1 Gravimetric method - The first flask contains the sediment sample or standard. The second flask contains 175-200 mL of potassium hydrogen phthalate reagent as an HCl trap. The third and fourth flasks contain 175-200 mL of silver nitrate reagent. The second flask is a gas washing bottle and the third and fourth flasks are impingers.

- 13.1.2 Colorimetric method - The first flask contains the sediment sample or standard. The second and third flask contain an absorbant of 80 mL 0.5M NaOH reagent. The second and third flasks are impingers.
- 13.1.3 Ion-selective electrode method - The first flask contains the sediment sample or standard. The second and third flask contain an absorbant of 50 mL SAOB reagent and 30 mL DDIW. The second and third flasks are impingers.
- 13.2 One hundred milliliters (100 mL) of DDIW, minus the volume of water contained in the wet sediment sample in Section 13.3, and a magnetic stirring bar are added to the flask that will contain the sediment. For the computation of the volume of water contained in the wet sediment, see Section 15.3. The traps are filled and deaerated by bubbling nitrogen for 10 minutes at a flowrate of 100 cm³/min. Reduce flow to 40 cm³/min.
- 13.3 Weigh approximately 10 g of wet sediment. If AVS concentration is high, a smaller amount of sediment may be required; use of sediment samples smaller than 1-2 grams is not recommended due to sulfide oxidation and sample heterogeneity. Use of large sediment samples is not recommended because significant amounts of acid may be neutralized. Place sediment in the standard taper round bottom flask or the Erlenmeyer flask fitted with the thistle tube or separatory funnel. Parafilm has been found to be free of sulfide. Samples may be weighed on 2 x 2 inch pieces of parafilm and the parafilm and sample introduced to the flask. Rinsing the sample into the flask is not recommended. Purge the sample for 10 minutes at a nitrogen flowrate of 40 cm³/min. Stop the flow of nitrogen.
- 13.4 Using a 30 mL syringe, inject 20 mL of 6M HCl, which has been bubbled with N₂ gas for 30 minutes, into the reactor through the septum. If the apparatus described in Section 6.1.1.1 is used, add the HCl from the thistle tube or the separatory funnel. Bubble N₂ through the sample for 1 hour at a flowrate of 20 cm³/min and magnetically stir the sample at the same time.
- 13.5 Analyze sulfide contained in sulfide trap by the appropriate analytical procedure in Section 14.

14.0 ANALYSIS OF SULFIDE

14.1 Gravimetric method

- 14.1.1 Insure that the final trap, the second silver nitrate trap, contains no precipitate.
- 14.1.2 Filter the silver sulfide contained in the first sulfide trap through a preweighed 1.2 micron filter. Dry at 102E C and weigh.
- 14.1.3 Calculate the amount of silver sulfide as the difference between the weight of silver sulfide and the filter and the weight of the predried filter.
- 14.1.4 Calculate the amount of sulfide in the sample:
$$\text{Sulfide in wet sediment } (\mu\text{moles}) = \text{g Ag}_2\text{S} / 247.8 \times 10^6$$

14.2 Colorimetric method

- 14.2.1 If the AVS concentration is low, add 10 mL of the mixed diamine reagent (MDR) directly to the NaOH solution in each trap tube to develop the color. Transfer this solution to a 100 mL volumetric flask and dilute to the mark with DDIW. If the sulfide contained in the NaOH in the tube trap exceeds 18 μmoles , transfer the NaOH in each tube trap to a 100 mL volumetric flask. Rinse the trap with deaerated 0.5M NaOH and dilute to volume with NaOH. An appropriate volume aliquot of this solution is used for the analysis. In this case, the aliquot is transferred to a 100 mL. Sufficient 0.5M NaOH is added so that the total volume is 80 mL, 10 mL MDR is added and the solution is diluted to 100 mL with DDIW. Use of sediment samples smaller than 1-2 grams is not recommended due to sulfide oxidation and sample heterogeneity.
- 14.2.2 After 30 minutes, measure the absorbance of light at 670 nm using a half-inch diameter or 1 cm rectangular spectrophotometer cell.
- 14.2.3 If the absorbance of the sample is greater than 0.6, dilute 10-fold with 1.0M H_2SO_4 and compare to the high range calibration curve.

14.2.4 Normally, the sulfide concentration in second trap tube is close to the blank value in this procedure and is not significant in calculating the concentration of sulfide. If a significant color is developed, the flow rate and amount of sulfide in the standard or sediment should be checked.

14.2.5 Preparation of calibration curve - The indicated amounts of sulfide are based on a 0.05M concentration of the sulfide stock standard solution. The procedure indicated in Section 14.1.4 should be used to calculate the exact amount of sulfide in each of the standards.

14.2.5.1 Low range calibration curve - 0.0 - 2.5 umoles S^{2-} (0.0 - 80 ug S^{2-})

Add 80 mL 0.5N sodium hydroxide to each of a series of 100 mL of flasks and add 0.00, 1.00, 2.00, 3.00, 4.00, and 5.00 mL of sulfide working standard A to these flasks. These samples contain 0.00, 0.50, 1.00, 1.50, 2.00, and 2.50 μ moles S^{2-} , respectively. Add 10.0 mL of MDR to each and dilute to 100.00 mL with deionized water. After 30 minutes, measure the absorbance at 670 nm.

14.2.5.2 High range calibration curve - 0.0 - 20.0 umoles S^{2-} (0.0 - 640 ug S^{2-})

Add 80 mL of 0.5M sodium hydroxide in 100 mL flasks and add 0.00, 1.00, 2.00, 3.00, and 4.00 mL of sulfide working standard B to these flasks. These samples contain 0.0, 5.00, 10.00, 15.00, and 20.00 umoles S^{2-} , respectively. Add 10.0 mL of MDR and dilute to 100.00 mL with deionized water. After 30 minutes, dilute the solution 10-fold with 1.0M H_2SO_4 , and measure the absorbance at 670 nm.

14.2.6 Calculate the amount of sulfide (umoles) in the sample from the calibration curve. If the total volume of NaOH in the trap was not used in the analysis, account for the portion tested.

14.3 Ion-selective electrode method

14.3.1 Calibrate the sulfide electrode and meter according to manufacturer's recommendations, using sulfide standards prepared in SAOB reagent diluted 1:1 with DDIW.

- 14.3.2 Transfer the contents of each sulfide trap into a 100-mL volumetric flask. Rinse the trap with DDIW, adding the rinses to the volumetric flask. Dilute to volume with DDIW.
- 14.3.3 Pour contents of volumetric flask into a 150-mL beaker, add a stirring bar and place on stirrer. Begin stirring with minimum agitation to avoid entrainment of air into the solution and minimize oxidation of the sample during the measurement.
- 14.3.4 Rinse sulfide and reference electrodes into waste container and blot dry with absorbent tissue. Immerse electrodes in sample solution.
- 14.3.5 Allow electrode response to stabilize (8-10 minutes), then take measurement of sulfide concentration. Depending on the meter used, the reading may be directly in concentration units if the meter is in the concentration mode and 2-point calibration has been performed. If the readings are in millivolts, convert millivolts to concentration using the calibration curve obtained from standard solutions.
- 14.3.6 Calculate the amount of sulfide (μmoles) in the sample.

15.0 CALCULATION OF AVS CONCENTRATION IN SEDIMENTS

- 15.1 The sediment dry weight/wet weight ratio (R) must be determined separately. Acid volatile sulfides can be oxidized or altered to non-volatile forms during drying.
- 15.2 Transfer an aliquot of the sediment to a tared 100-mL tared evaporating dish. Weigh the dish plus the wet sediment. Calculate the wet weight of the sample. Dry the sediment at 104°C and weigh. Calculate the dry weight of sediment.
- 15.3 Determine the ratio of dry weight to wet weight for the sediment sample:

$$R = W_d / W_w$$

where

$$\begin{aligned} R &= \text{ratio of dry weight to wet weight} \\ W_d &= \text{dry weight of sediment sample (g), and} \end{aligned}$$

W_w = wet weight of sediment sample (g).

Also, the weight of water, W_{water} taken in a sample for AVS analysis can be calculated. If the weight of the wet sediment sample taken for the AVS analysis is $W_{\text{S+W}}$, the weight of water contained in the sediment sample would be

$$W_{\text{water}} = W_{\text{S+W}} - (R \times W_{\text{S+W}})$$

The volume of water in the sample equals the weight of water, assuming the density is near unity.

- 15.4 Compute the sulfide concentration per gram dry weight of sediment:

$$\text{AVS } (\mu\text{moles/g}) = S / R \times W_w$$

where

S = the amount of AVS in sediment (μmoles)
 R = ratio of dry weight to wet weight
 W_w = wet weight of sediment (g) taken from AVS analysis.

The QC data obtained during the analysis provides an indication of the quality of the sample data and should be provided with the sample results.

16.0 DETERMINATION OF SIMULTANEOUSLY EXTRACTED METALS (SEM)

- 16.1 After the generation of sulfide has been completed, filter the sediment suspension remaining in the H_2S generation flask through a 0.2 μ membrane filter resistant to attack by acid.
- 16.2 Transfer the solution to a 250 mL volumetric flask. Rinse the filtering flask with distilled water, adding the rinses to the volumetric flask. Dilute to volume with deionized water.
- 16.3 Determine the concentrations of cadmium, copper, mercury, nickel, lead and zinc by atomic absorption, inductive coupled plasma spectrometric, or another approved method. Convert $\mu\text{g/L}$ concentration values to $\mu\text{moles/L}$. Multiply the $\mu\text{moles/L}$ by the solution volume to obtain the μmoles of metal.

16.4 Report the concentrations of each of the metals in the sediment of a umole per gram dry sediment (umol/g) basis.

16.5 Calculate the ratio of SEM to AVS:

$$\text{SEM} / \text{AVS} = [\text{metal}] / \text{AVS}$$

where

SEM = the sum of the concentrations of metals

[metal]= the metals cadmium, copper, lead, mercury, nickel, lead and zinc

AVS = acid volatile sulfide concentration determined

Both SEM and AVS are expressed on a umole per gram dry sediment (umol/g) basis.

16.6 A SEM-AVS ratio greater than one suggests that toxicity is possible while a ratio less than one suggests that the metals in the sediment are not toxic.

17.0 REFERENCES

- 17.1 Cornwell, J.C. and J.W. Morse, "The Characterization of Iron Sulfide Minerals in Anoxic Marine Sediments", *Marine Chemistry*, 1987, 22, 193-206.
- 17.2 DiToro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mayr and M.S. Redmond, "Toxicity of Cadmium in Sediments: The Role of Acid Volatile Sulfide", *Environmental Toxicology and Chemistry*, 1990, 9, 1487-1502.
- 17.3 Morse, J.W., F.J. Millero, J.C. Cornwell and d. Richard, "The Chemistry of the Hydrogen Sulfide and Iron Sulfide System in Natural Waters", *Earth Science Review*, 1987, 24, 1-42.
- 17.4 Allen, H.E., G. Fu and B. Deng, "Determination of Acid Volatile Sulfide (AVS) in Sediment", Report to Environmental Protection Agency Office of Water Regulations and Standards, Washington, December 1990, 26 pages.
- 17.5 Boothman, W.S., "Acid-volatile Sulfide Determination in Sediments Using Sulfide-specific Electrode Detection", U.S. Environmental Protection Agency Environmental Research Laboratory, Narragansett, R.L., undated, 8 pages.

- 17.6 Baumann, E.W., Analytical Chemistry, 1974, 46, 1345-1347.
- 17.7 U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, revised March 1983.
- 17.8 "Standard Methods for the Examination of Water and Wastewater", 17th edition, APHA, AWWA, WPCF, 1989.
- 17.9 Rapin, F., A. Tessier, P.G.C. Campbell and R. Carignan, "Potential Artifacts in the Determination of Metal Partitioning in Sediments by a Sequential Extraction Procedure", Environmental Science and Technology, 1986, 20, 836-840.
- 17.10 Code of Federal Regulations 40, ch. 1, Pt, 136, Appendix B.

18.0 RECORDS AND REPORTING

- 18.1 Records are maintained as required by contract/solicitation.
- 18.2 All analyses are reported in accordance with client/contract requirements.