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FINAL UNIFORM FEDERAL POLICY SAMPLING AND ANALYSIS PLAN FOR SITE INSPECTION OF THE SKEET RANGE UXO 2 NAS CORPUS CHRISTI TX

07/01/2009

TETRA TECH NUS, INC

Comprehensive Long-term Environmental Action Navy

CONTRACT NUMBER N62467-04-D-0055

Rev. 0
07/22/09

Final
Uniform Federal Policy
Sampling and Analysis Plan
for
Site Inspection of the Skeet Range

Naval Auxiliary Landing Field Waldron
Corpus Christi, Texas

Contract Task Order 0115

July 2009

NAS Jacksonville
Jacksonville, Florida 32212-0030

TETRA TECH NUS, Inc.

SAP Worksheet No. 1 -- Title and Approval Page

(UFP QAAP Manual Section 2.1)

Final
Uniform Federal Policy
Sampling and Analysis Plan
for
Site Inspection of the Skeet Range
Naval Auxiliary Landing Field Waldron
Corpus Christi, Texas

July 2009

Prepared for:
Naval Facilities Engineering Command Southeast
NAS Jacksonville
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Prepared under:
CONTRACT NUMBER N62467-04-D-0055
CONTRACT TASK ORDER 0115

Review Signatures

_____	_____
G. KENNETH GRIM, JR. P.G. DATE	KELLY CARPER DATE
TASK ORDER MANAGER	CLEAN QA MANAGER
TETRA TECH NUS, INC.	TETRA TECH NUS, INC.
HOUSTON, TEXAS	PITTSBURGH, PENNSYLVANIA

Approval Signatures

_____	_____
HELEN LOCKARD DATE	KENNETH BOWERS DATE
REMEDIAL PROJECT MANAGER	NAVFAC CHEMIST
NAVFAC SE	NAVFAC QAO

EXECUTIVE SUMMARY

Tetra Tech NUS, Inc. (TtNUS) has prepared this Sampling and Analysis Plan (SAP) under the Comprehensive Long-Term Environmental Action Navy (CLEAN) Contract No. N62467-04-D-0555, Contract Task Order (CTO) 0115.

Naval Auxiliary Landing Field (NALF) Waldron is an outlying field (OLF) that supports Naval air training operations out of Naval Air Station Corpus Christi (NASCC). NASCC, home to the Chief of Naval Air Training (CNATRA), maintains and operates facilities and provides services and material to support operations of aviation facilities of the Naval Air Training Command and other tenant activities. The general command assignment is pilot training, primarily focusing on primary and intermediate flight maneuvering and traffic pattern operations. Training Air Wing FOUR based at the main installation performs touch-and-go landing training between the main installation and NALF Waldron, 3 miles south of NASCC.

The former Skeet Range, constructed in March 1945, encompasses approximately 8.6 acres and was located in the northwestern corner of NALF Waldron. The Skeet Range was used for cadet and security personnel weaponry training and qualification, moving target orientation training of Naval aviators, and likely for recreation. The Skeet Range was comprised of three firing arcs facing north toward the installation fenceline. It included “high” and “low” skeet houses positioned at the end of each arc. Ammunition used at the site likely included 12-, 16-, and 20-gage and .410 caliber shotgun munitions and possibly other small arms ammunition. The range was demolished sometime between June 1947 and July 1961. The area is currently open land covered with vegetation and not used for weaponry training purposes. Future use is not expected to change.

As a result of the Navy’s munitions training activities, Munitions Constituents (MC) may be present at the NALF Waldron Skeet Range. Munitions and Explosives of Concern (MEC) are not suspected to be present. The term MEC includes Discarded Military Munitions (DMM), Unexploded Ordnance (UXO), and MC in high enough concentrations to pose an explosive hazard. The Navy is following the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process for the investigation of this site.

The initial phase of the CERCLA process, the Preliminary Assessment (PA), was completed in April 2005 and identified the skeet range or Munitions Response Area or Munitions Response Site (MRA/S) at NALF Waldron for further investigation. The PA used five primary sources of information to support the facility data collection effort, including historical archives, personal interviews, installation data repositories

(including the Administrative Record), visual surveys, and off-facility data sources and repositories such as local libraries and museums.

The primary objective of this Munitions Response Program (MRP) MRA/S Site Inspection (SI) is to determine if further CERCLA response actions or Remedial Investigations (RI) are appropriate for the Skeet Range. The SI considers the background information provided in the PA and includes collection of supplemental site-specific environmental data to further define the nature and extent of MC at the Skeet Range. The SI is a secondary component of the CERCLA site evaluation process and is not intended to be a full-scale study of the nature and extent of contamination. This SI consists of a focused sampling and analysis program designed to identify potential contaminants based on information in the PA and various Navy and regulatory guidance for investigation of skeet ranges.

The information provided in the worksheets making up this Uniform Federal Policy (UFP) Quality Assurance Project Plan (QAPP) was developed based on the results of project scoping meetings among the planning team, which consists of representatives of the Navy, United States Environmental Protection Agency (USEPA), Texas Commission on Environmental Quality (TCEQ), and TtNUS (See Worksheet No. 9 for attendees). Appendix A contains the general and site-specific Conceptual Site Model (CSM) for the site. The CSM was used as the basis for development of the site-specific project Data Quality Objectives (DQOs), which are contained in Worksheet No. 11. The remainder of the worksheets describe the sampling, analytical, and data evaluation procedures, including quality requirements.

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ACRONYMS

ARAR	Applicable or Relevant and Appropriate Requirement
ASAP	As Soon As Possible
BERA	Baseline Ecological Risk Assessment
bgs	Below ground surface
° C	Degree Celsius
C	Carcinogen
CA	Corrective Actions
CAS	Chemical Abstracts Service
CCC	Calibration Check Compound
CCB	Continuing Calibration Blank
CCV	Continuing Calibration
CEC	Cation Exchange Capacity
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CHSO	Company Health and Safety Officer
CLEAN	Comprehensive Long-Term Environmental Action Navy
CLP	Contract Laboratory Program
CNATRA	Chief of Naval Air Training
COC	Chemical of Concern
COPC	Contaminant of Potential Concern
CSM	Conceptual Site Model
CTC	Cost to Complete
CTO	Contract Task Order
DFTPP	Decafluorotriphenylphosphine
DoD	Department of Defense
DMM	Discarded Military Munitions
DQI	Data Quality Indicator
DQO	Data Quality Objective
DVM	Data Validation Manager
EPA Eco-SSL	EPA Ecological Soil Screening Level
ESS	Explosives Safety Submission
° F	Degree Fahrenheit
FID	Flame Ionization Detector

FOL	Field Operations Leader
FPXRF	Field Portable X-Ray Fluorescence
FS	Feasibility Study
FTMR	Field Task Modification Request
FUDS	Formerly Used Defense Site
GC	Gas Chromatography
GIS	Geographic Information System
GPS	Global Positioning System
HASP	Health and Safety Plan
HSM	Health and Safety Manager
ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma
IDW	Investigative-Derived Waste
INRPM	Integrated Natural Resources Management Plan
IRCDQM	Navy Installation Restoration Chemical Data Quality Manual
IS	Internal Standard
LBGR	Lower Bound of the Gray Region
LCS	Laboratory Control Sample
LCSD	Laboratory Control Spike Duplicate
LIMS	Laboratory Information Management Systems
MC	Munitions Constituents
MDL	Method Detection Limit
MEC	Munitions and Explosives of Concern
mg/kg	Milligram per kilogram
mg/L	Milligram per liter
MMRP	Military Munitions Response Program
MPC	Measurement Performance Criteria
MRP	Munitions Response Program
MRA/S	Munitions Response Area or Munitions Response Site
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MS	Mass spectrometer
NA	Not Applicable or Not Available
NAAS	Naval Air Auxiliary Station
NALF	Navy Auxiliary Landing Field
NAS	Naval Air Station
NASCC	Naval Air Station Corpus Christi

NAVFAC SE	Naval Facilities Engineering Command Southeast
NC	Non-Carcinogen
NCP	National Contingency Plan
NELAP	National Environmental Laboratory Accreditation Program
NFA	No Further Action
NFESC	Naval Facilities Engineering Service Center
NIST	National Institute of Standards and Technology
OE	Ordnance and Explosives
OLF	Outlying field
OSHA	Occupational Safety and Health Administration
Oz	Ounce
PA	Preliminary Assessment
PAH	Polynuclear aromatic hydrocarbons
PARCC	Precision, Accuracy, Representativeness, Completeness, and Comparability
PCL	Protective Concentration Level
PG	Professional Geologist
PM	Project Manager
PMO	Project Management Office
POC	Point of Contact
PPE	Personal Protective Equipment
PQL	Project Quantitation Limit
PQLG	Project Quantitation Limit Goal
PT	Proficiency Testing (previously known as performance evaluation [PE] sample)
QA	Quality assurance
QAM	Quality Assurance Manager
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QC	Quality control
QL	Quantitation Limit
QSM	Quality Systems Manual
%R	Percent Recovery
RAGS	Risk Assessment Guidance for Superfund
RBSL	Risk based screening level
RCI	Reactivity, corrosivity, and ignitability
RF	Response Factor
RI	Remedial Investigation

RPD	Relative Percent Difference
RPM	Remedial Project Manager
RSD	Relative standard deviation
SAP	Sampling and Analysis Plan
SDG	Sample Delivery Group
SDZ	Surface Danger Zone
SI	Site Inspection
SOP	Standard Operating Procedure
SPCC	System performance Check Compound
SSO	Site Safety Officer
TAL	Target Analyte List
TCLP	Toxicity Characteristic Leaching Procedure
TCEQ	Texas Commission on Environmental Quality
TPH	Total Petroleum Hydrocarbons
TOC	Total organic carbon
TOM	Task Order Manager
TtNUS	Tetra Tech NUS, Inc.
TRRP	Texas Risk Reduction Program
TtNUS	Tetra Tech NUS, Inc.
TXERA	Texas Ecological Risk Assessment Guidance
ug/dL	Micrograms per deciliter
UFP	Uniform Federal Policy
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
UXO	Unexploded Ordnance
VOA	Volatile organic analysis
VOC	Volatile organic compounds
VSP	Visual Sample Plan
WWII	World War II
Wt	Weight
XRF	X-ray fluorescence

SAP Worksheet No. 2 -- SAP Identifying Information

Site Name/Number:	**Skeet Range at Naval Auxiliary Landing Field Waldron, Corpus Christi, Texas**
Operable Unit:	**N/A**
Contractor Name:	**Tetra Tech NUS, Inc.**
Contract Number:	**N62467-04-D-0055**
Contract Title:	**CLEAN IV**
Work Assignment Number (optional):	**CTO 0115**

1. This SAP was prepared in accordance with the requirements of the *Uniform Federal Policy for Quality Assurance Plans (UFP-QAPP)* (USEPA 2005) and *EPA Guidance for Quality Assurance Project Plans, EPA QA/G-5, QAMS (*USEPA 2002*)*.

2. Identify regulatory program: Munitions Response Program (MRP); National Contingency Plan (NCP); Comprehensive Environmental Response Compensation, and Liability Act of 1980 (CERCLA)

3. This SAP is a project-specific Sampling and Analysis Plan (SAP).

4. List dates of scoping sessions that were held:

Scoping Session	Date
Kick-off meeting for development of CSM and DQOs	August 27, 2008

5. List dates and titles of any SAP documents written for previous site work that are relevant to the current investigation.

Title	Date
Not Applicable (NA) – Initial MRP SI	

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

USEPA Region 6 – Regulatory Oversight
TCEQ – Regulatory Oversight
Naval Facilities Engineering Command Southeast (NAVFAC SE) – Property Owner

7. Lead organization Naval Facilities Engineering Command Southeast

8. If any required SAP elements or required information are not applicable to the project or are provided elsewhere, then note the omitted SAP elements and provide an explanation for their exclusion below:

UFP QAPP Worksheet No.	Required Information	Crosswalk to Related Information
A. Project Management		
Documentation		
1	Title and Approval Page	NA
2	Table of Contents SAP Identifying Information	NA
3	Distribution List	NA
4	Project Personnel Sign-Off Sheet	NA
Project Organization		
5	Project Organizational Chart	NA
6	Communication Pathways	NA
7	Personnel Responsibilities and Qualifications Table	NA
8	Special Personnel Training Requirements Table	NA
Project Planning/ Problem Definition		
9	Project Planning Session Documentation (including Data Needs tables) Project Scoping Session Participants Sheet	NA
10	Problem Definition, Site History, and Background. Site Maps (historical and present)	NA
11	Site-Specific Project Quality Objectives	NA
12	Measurement Performance Criteria Table	NA
13	Sources of Secondary Data and Information Secondary Data Criteria and Limitations Table	NA
14	Summary of Project Tasks	NA
15	Reference Limits and Evaluation Table	NA
16	Project Schedule/Timeline Table	NA
B. Measurement Data Acquisition		
Sampling Tasks		
17	Sampling Design and Rationale	NA
18	Sampling Locations and Methods/SOP Requirements Table Sample Location Map(s)	NA
19	Analytical Methods/SOP Requirements Table	NA
20	Field Quality Control Sample Summary Table	NA
21	Project Sampling SOP References Table Sampling SOPs	NA
22	Field Equipment Calibration, Maintenance, Testing, and Inspection Table	NA
Analytical Tasks		
23	Analytical SOPs Analytical SOP References Table	NA
24	Analytical Instrument Calibration Table	NA
25	Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	NA
Sample Collection		
26	Sample Handling System, Documentation Collection, Tracking, Archiving and Disposal Sample Handling Flow Diagram	NA
27	Sample Custody Requirements, Procedures/SOPs Sample Container	NA

UFP QAPP Worksheet No.	Required Information	Crosswalk to Related Information
	Identification Example Chain-of-Custody Form and Seal	
Quality Control Samples		
28	QC Samples Table Screening/Confirmatory Analysis Decision Tree	NA
Data Management Tasks		
29	Project Documents and Records Table	NA
30	Analytical Services Table Analytical and Data Management SOPs	NA
C. Assessment Oversight		
31	Planned Project Assessments Table Audit Checklists	NA
32	Assessment Findings and Corrective Action Responses Table	NA
33	QA Management Reports Table	NA
D. Data Review		
34	Verification (Step I) Process Table	NA
35	Validation (Steps IIa and IIb) Process Table	NA
36	Validation (Steps IIa and IIb) Summary Table	NA
37	Usability Assessment	NA

SAP Worksheet No. 3 -- Distribution List

(UFP-QAPP Manual Section 2.3.1)

Name of SAP Recipient	Title/Role	Organization	Telephone Number (Optional)	E-Mail Address or Mailing Address	Document Control Number (Optional)
Helen Lockard	Remedial Project Manager (RPM)	NAVFAC SE	904-542-6858	helen.lockard@navy.mil	NA
Dalton Shaughnessy	RPM	NAVFAC SE	904-542-6961	Dalton.shaughnessy@navy.mil	NA
Gary LeFlore	Base Coordinator	NASCC	361-961-5354 Cell: 361-633-9151	gary.leflore@navy.mil	NA
G. Kenneth Grim, Jr.	Task Order Manager (TOM)	TtNUS	832-251-6023	kenneth.grim@tetratech.com	NA
Mark Perry	Project Management Office (PMO)	TtNUS	412-921-7217	mark.perry@tetratech.com	NA
Chris Siegel	TCEQ Representative	TCEQ	512-239-2992	csiegel@tceq.state.tx.us	NA
Rich Mayer	USEPA Region 6 Representative	USEPA	214-665-7440	mayer.richard@epa.gov	NA
Larry Basilio	Field Operations Leader (FOL)/Site Safety Officer (SSO)/Senior Geologist	TtNUS	832-251-6018	larry.basilio@tetratech.com	NA
Matthew Kraus	Project Chemist	TtNUS	412-921-8729	matthew.kraus@tetratech.com	NA
Janice Shilling	Laboratory Project Manager (PM)	Empirical Laboratory	615-345-1119	jshilling@empirlabs.com	NA
Michelle Johnston	Laboratory Project Manager (PM)	Test America	303-736-0100	Michelle.johnston@ Testamericainc.com	NA

SAP Worksheet No.4 -- Project Personnel Sign-Off Sheet

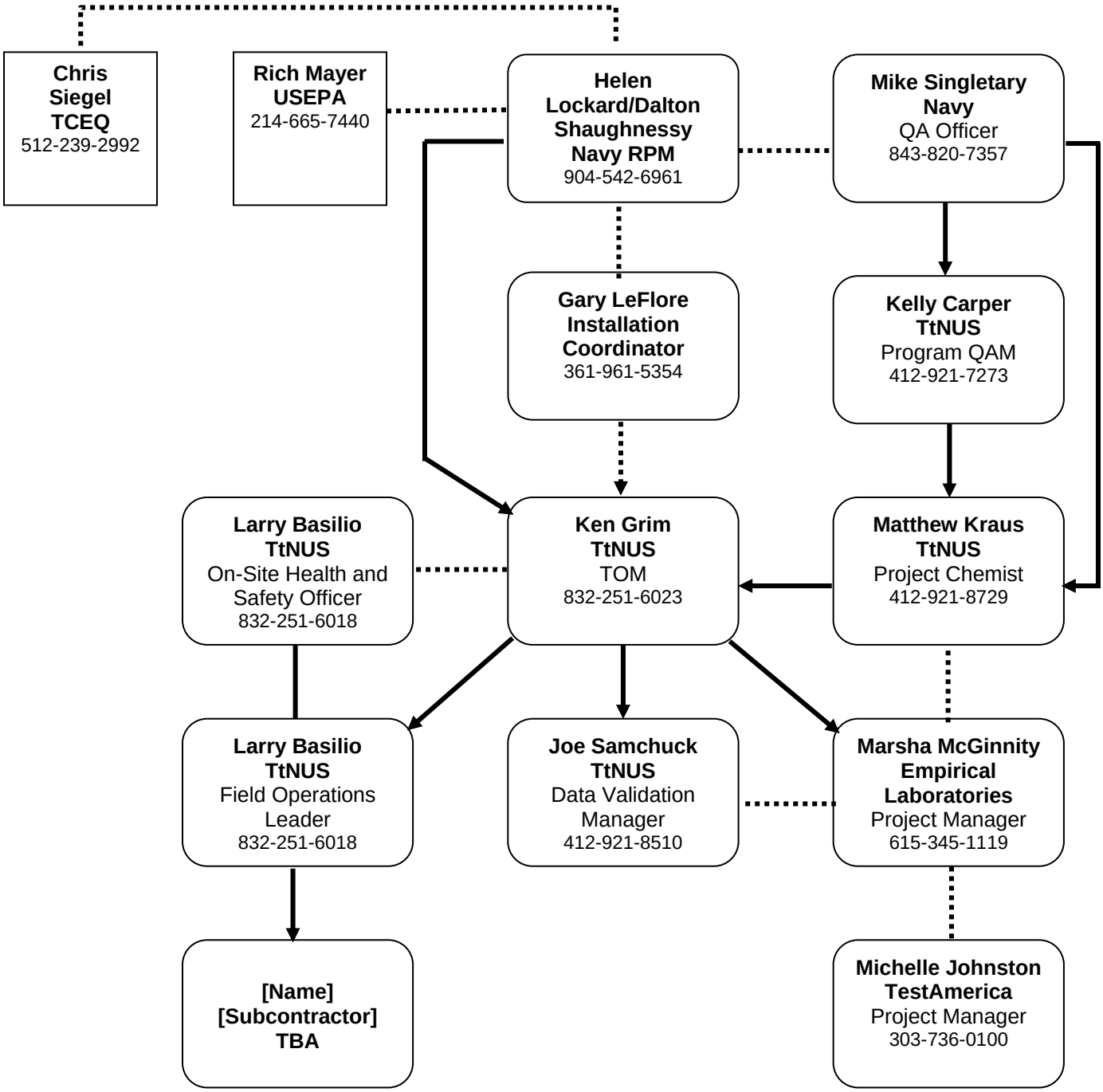
(UFP-QAPP Manual Section 2.3.2)

Name	Organization/Title/Role	Telephone Number (optional)	Signature/E-Mail receipt	SAP Section Reviewed	Date SAP Read
Helen Lockard	NAVFAC SE/RPM	904-542-6858	helen.lockard@navy.mil		
Dalton Shaughnessy	NAVFAC SE/RPM	904-542-6961	Dalton.shaughnessy@navy.mil		
Gary LeFlore	NASCC Environmental/Base Coordinator	361-961-5354 Cell: 361-633-9151	gary.leflore@navy.mil		
G. Kenneth Grim, Jr.	TtNUS/P.G./TOM	832-251-6023	kenneth.grim@tetratech.com		
Larry Basilio	TtNUS/FOL/SSO/Senior Geologist	832-251-6018	larry.basilio@tetratech.com		
Kelly Carper	TtNUS/Program Quality Assurance Manager (QAM)	412-921-7273	kelly.carper@tetratech.com		
Matt Soltis	TtNUS/Health and Safety Manager (HSM)	412-921-8912	matt.soltis@tetratech.com		
Joseph Samchuck	TtNUS/Data Validation Manager (DVM)	412-921-8510	joe.samchuck@tetratech.com		
Janice Shilling	Empirical Laboratories/PM	615-345-1119	Jshilling@EmpirLabs.com		
Michelle Johnston	TestAmerica/PM	303-736-0100	Michelle.johnston@ Testamericainc.com		
Matthew Kraus	TtNUS/Project Chemist	412-921-8729	matthew.kraus@tetrtech.com		

SAP Worksheet No. 5 -- Project Organizational Chart

(UFP-QAPP Manual Section 2.4.1)

Lines of Authority ——— Lines of Communication ·····



SAP Worksheet No. 6 -- Communication Pathways

(UFP-QAPP Manual Section 2.4.2)

Communication Driver	Responsible Affiliation	Name	Phone Number and/or E-Mail	Procedure (timing, pathway to & from, etc.)
SAP Amendments	TtNUS TOM	G. Kenneth Grim, Jr.	832-251-6023	Immediately informs Navy Document via Field Task Modification Request (FTMR) form.
Changes in Schedule	TtNUS TOM	G. Kenneth Grim, Jr.	832-251-6023	Informs Navy via schedule impact letter as soon as impact is realized.
Issues in the field that result in changes in scope of field work	TtNUS FOL TtNUS TOM TtNUS DVM	Larry Basilio G. Kenneth Grim, Jr. Joe Samchuck	832-251-6018 832-251-6023 412-921-8510	FOL informs TOM; TOM informs RPM; RPM issues scope change if warranted. Scope change to be implemented before work is executed. Document via FTMR form.
Recommendations to stop work and initiate work upon corrective action	TtNUS FOL TtNUS TOM TtNUS QAM TtNUS HSM Navy RPM Navy RPM	Larry Basilio G. Kenneth Grim, Jr. Kelly Carper Matt Soltis Helen Lockard Dalton Shaugnessy	832-251-6018 832-251-6023 412-921-7273 412-921-8912 904-542-6858 904-542-6961	Responsible party immediately informs subcontractors, the Navy, and Project Team.
Analytical data quality issues	Empirical Laboratory PM Testamerica PM TtNUS Project Chemist	Janice Shilling Michelle Johnston Matt Kraus	615-345-1119 303-736-0100 412-921-8729	Immediately notify TtNUS Project Chemist and TtNUS TOM. Notify data validation staff if necessary.

SAP Worksheet No. 7 – Personnel Responsibilities and Qualifications Table

(UFP-QAPP Manual Section 2.4.3)

Name	Title/Role	Organizational Affiliation	Responsibilities	Education and/or Experience Qualifications (Optional)
Kenneth Grim	TOM	TtNUS	Oversees project, financial, schedule, and technical day-to-day management of the project. • Ensures timely resolution of project-related technical, quality, and safety questions associated with TtNUS operations. • Functions as the primary TtNUS interface with the Navy RPM, NALF Waldron, TtNUS field and office personnel, and laboratory points of contact. • Ensures that TtNUS health and safety issues related to this project are communicated effectively to all personnel and off-site laboratories. • Monitors and evaluates all TtNUS subcontractor performance. • Coordinates and oversees work performed by TtNUS field and office technical staff (including data validation, data interpretation, and report preparation). • Coordinates and oversees maintenance of all TtNUS project records. • Coordinates and oversees review of TtNUS project deliverables. • Prepares and issues final TtNUS deliverables to the Navy.	M.S. Geology, 17 years environmental experience. Licensed Texas Geoscientist.

Name	Title/Role	Organizational Affiliation	Responsibilities	Education and/or Experience Qualifications (Optional)
Larry Basilio	FOL, SSO	TtNUS	Supervises, coordinates, and performs field sampling activities • Ensures that all health and safety requirements unique to the SI are implemented. • Functions as the on-site communications link between field staff members, the SSO, NALF Waldron, and TtNUS TOM. • Alerts off-site analytical laboratories of any special health and safety hazards associated with environmental samples. • Oversees the mobilization and demobilization of all field equipment and subcontractors. • Coordinates and manages the field technical staff. • Adheres to the work schedules provided by the TtNUS TOM. • Ensures the proper maintenance of site logbooks, field logbooks, and field recordkeeping. • Initiates field task modification requests (field change orders) when necessary. • Identifies and resolves problems in the field, resolving difficulties via consultation with NALF Waldron personnel, implements and documents corrective action procedures, and provides communication between the field team and project management.	B.S. Geology, 25 years environmental experience. Licensed Texas Geoscientist.

Name	Title/Role	Organizational Affiliation	Responsibilities	Education and/or Experience Qualifications (Optional)
Kelly Carper	QAM	TtNUS	Reviews QAPP, oversees preparation of laboratory scope, coordinates with laboratory, and conducts data quality reviews. Ensures quality aspects of the CLEAN program. • Develops, maintains, and monitors quality assurance (QA) policies and procedures. • Provides training to TtNUS staff in quality assurance/quality control (QA/QC) policies and procedures. • Conducts systems and performance audits to monitor compliance with environmental regulations, contractual requirements, QAPP requirements, and corporate policies and procedures. • Audits project records. • Monitors subcontractor quality controls and records. • Assists in the development of corrective action plans and ensuring correction of non-conformances reported in internal or external audits. • Ensures that this SAP meets TtNUS, Navy, and TCEQ requirements. • Prepares QA reports for management.	B.S. Biology, 16 years environmental experience.

Name	Title/Role	Organizational Affiliation	Responsibilities	Education and/or Experience Qualifications (Optional)
Matt Kraus	Project Chemist	TtNUS	Coordinates analyses with laboratory chemists, ensures that the scope is followed, QA data packages, and communicates with TtNUS staff. • Ensures that the project meets objectives from the standpoint of laboratory performance. • Provides technical advice to the TtNUS team on matters of project chemistry. • Monitors and evaluates subcontractor laboratory performance. • Ensures timely resolution of laboratory-related technical, quality, or other issues effecting project goals. • Functions as the primary interface with the subcontracted laboratory and the TtNUS TOM. • Coordinates and oversees work performed by the subcontracted laboratory. • Oversees the completion of TtNUS data validation. • Coordinates and oversees review of laboratory deliverables. • Recommends appropriate laboratory corrective actions.	B.S. Environmental Chemistry, 4 years environmental experience.
Joseph Samchuck	DVM	TtNUS	Quality assurance of data validation deliverables.	B.S. Chemistry, MBA, M.S. Finance, 23 years environmental experience.
Janice Shilling	Chemical Laboratory PM	Empirical Laboratories	Coordinates analyses with laboratory chemists, ensures that scope is followed, QAs data packages, and communicates with TtNUS staff	Can be provided upon request.
Michelle Johnston	Chemical Laboratory PM	TestAmerica	Coordinates analyses with laboratory chemists, ensures that scope is followed, QAs data packages, and communicates with TtNUS staff	Can be provided upon request.

Name	Title/Role	Organizational Affiliation	Responsibilities	Education and/or Experience Qualifications (Optional)
Matt Soltis	HSM	TtNUS	Oversees CLEAN Program Health and Safety Program • Provides technical advice to the TtNUS TOM on matters of health and safety. • Oversees the development and review of the Health and Safety Plan (HASP). • Conducts health and safety audits. • Prepares health and safety reports for management.	B.S. Industrial Safety Sciences, 24 years environmental experience.

In some cases, one person may be designated responsibilities for more than one position. For example, the FOL may also be responsible for SSO duties. This action will be performed only as credentials, experience, and availability permits.

SAP Worksheet No. 8 -- Special Personnel Training Requirements Table

(UFP-QAPP Manual Section 2.4.4)

All field personnel will have appropriate training to conduct the field activities to which they are assigned. Additionally, each site worker will be required to have completed a 40-hour course (and 8-hour refresher, if applicable) in health and safety training as described under Occupational Safety and Health Administration (OSHA) 29 Code of Federal Regulations (CFR) 1910.120(b)(4). Safety requirements are addressed in greater detail in the accompanying TtNUS HASP.

The selected analytical laboratory (Empirical Laboratories) has successfully completed the laboratory approval process required as part of the Naval Facilities Engineering Service Center (NFESC) Quality Assurance Program and described in the Department of Defense Quality Systems Manual (DoD QSM) (January 2006).

SAP Worksheet No. 9 -- Project Scoping Session Participants Sheet

(UFP-QAPP Manual Section 2.5.1)

Project Name: NALF Waldron Projected Date(s) of Sampling: April 2009 Task Order Manager: G. Kenneth Grim, Jr.	Site Name: Skeet Range, NALF Waldron Site Location: Corpus Christi, Texas
Date of Session: August 27, 2008 **Scoping Session Purpose:** Data Quality Objective Session	

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
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Larry Basilio	FOL/Sr. Geologist	TtNUS	832-251-6018	larry.basilio@tetratech.com	Task Management/ Technical
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Comments/Decisions: A site walk was conducted by session participants. After the site walk was completed, the DQO session was held. The Conceptual Site Model was reviewed, and the Seven-step DQO process was then conducted for the site.

Action Items: Complete worksheets and text for work plan and implement review process.

Consensus Decisions: Worksheets will be completed by the most appropriate personnel and then reviewed by technical personnel and TtNUS Project Manager.

SAP Worksheet No. 10 -- Problem Definition, Site History and Background

(UFP-QAPP Manual Section 2.5.2)

The initial CSM for the Skeet Range at NALF Waldron presented in Appendix A, was developed as part of the PA (Malcolm Pirnie, 2005), which is one of the initial steps in the CERCLA process. The CSM includes a detailed history of NALF Waldron and the site. Background information on the general and site-specific environmental setting is also provided. The CSM will be updated as additional information is obtained. An updated version of the CSM, that incorporates the data obtained during the SI field effort, will be presented in the report prepared after all fieldwork is completed.

Appendix A provides general information on the site background, facility history, and general description of the geology, hydrology, endangered species, cultural settings, and natural resources on an installation-wide basis at NALF Waldron. A brief summary of the problem, which is based on the information presented in Appendix A, is presented below. This problem is Step 1 of the planning process and is referenced in Worksheet No. 11.

Skeet Range

The following is a ***summary*** of the problem definition for the Skeet Range that is detailed in Appendix A:

- Environmental contamination may exist at the Skeet Range (8.6 acres) because the facility was used as a skeet range (limited to shotguns and possibly small arms). Following construction of the range in March 1945, Naval aviation cadets, installation officers, enlisted men, and security personnel used the range for personnel weaponry training and qualification, Naval aviator moving target orientation training, and possibly recreation. The range was closed for weaponry training purposes and demolished sometime between June 1947 and July 1961. The installation Point of Contact (POC) indicated that the range was probably razed by bulldozing. There is currently no evidence of the former structures associated with the former Skeet Range. The range area has no current military use. Specific small arms ammunition types and materials used at the Skeet Range may have included 12,-, 16-, and 20- gauge, and .410 caliber shotgun munition shells. Based on the previous site usage, lead may have accumulated in soil over the years of operations.

- MC consisting of metals (primarily lead and, to a lesser extent, antimony, arsenic, copper, tin, and zinc) and polynuclear aromatic hydrocarbons (PAHs) (from pitch tar used in the clay pigeon

targets) may be present in site soil, particularly surface soil (0 to 1 foot below ground surface [bgs]), as a result of the military training activities. Lead is assumed to be the primary metal MC of concern in soil because it is the main constituent of the spent munitions and because of its documented toxicity to human and ecological receptors. It is anticipated that other metals contamination will be spatially correlated with lead concentrations because the release mechanisms and sources were the same for these chemicals. MC in surface soil may have migrated to subsurface soil and subsequently infiltrated to underlying groundwater. However, the nature and extent of potential environmental contamination at the Skeet Range is not known and must be investigated during this SI.

- The CSM (detailed in Appendix A) indicates that potentially complete exposure pathways exist for both human and ecological receptors under both current and hypothetical future land uses. However, potential human health and ecological risks have not been characterized for receptors exposed to the potentially contaminated environmental media. Unacceptable levels of human health and/or ecological risk may exist and must therefore be characterized during this SI.

SAP Worksheet No. 11. -- Project Quality Objectives/Systematic Planning Process

STATEMENTS FOR THE SKEET RANGE

PROBLEM DEFINITION (STEP 1)

Worksheet No. 10 contains the problem definition for the Skeet Range.

IDENTIFY THE GOALS OF THE STUDY (STEP 2)

The primary goals of this investigation of the Skeet Range are as follows:

1. Determine whether MC (specifically antimony, arsenic, lead, copper, tin, zinc, and PAHs) are present in study area surface soil at concentrations that exceed background concentrations and/or screening values. If surface soil concentrations at the Skeet Range exceed background concentrations and screening values, proceed to a Remedial Investigation (RI) and Feasibility Study (FS). Otherwise, recommend No Further Action (NFA).

2. Determine whether MC (specifically antimony, arsenic, lead, copper, tin, zinc, and PAHs) are present in study area soil at concentrations that exceed the criteria for protection of groundwater. If MC concentrations in surface soil exceed the criteria for protection of groundwater, recommend an investigation of groundwater. Otherwise, a groundwater investigation will not be initiated.

3. Collect data to begin delineation of the horizontal and vertical extent of surface soil contamination. If the data collected in the initial round of sampling are adequate to delineate the extent of surface soil contamination, stop delineation. Otherwise, return to the site during an RI to complete delineation of surface soil contamination.

All data collected for this project are expected to be transferable to support the following actions:

1. Update the Navy Cost to Complete (CTC) estimate.
2. Complete the site prioritization protocol.
3. Update the CSM using field data and initial risk screening results

IDENTIFY INFORMATION INPUTS (STEP 3)

Data required for making the decisions include the following:

1. Information from site-specific historical documents regarding site history (e.g., materials usage), any previous investigations (e.g., historical screening or fixed-base laboratory data), current/future site status (e.g., usage, topography, future plans for development, etc.). See Appendix A.

2. Field Screening Data: Lead will be analyzed in the field using a field portable x-ray fluorescence (XRF) detector. Field results will be used for delineation of soil contamination and for correlation to laboratory data. Because lead is the primary contaminant and other metals are expected to be co-located with lead, lead can be used as a marker for contamination. A value of 400 mg/kg will be used as the discriminator between contaminated and uncontaminated locations. The 400 mg/kg corresponds to the TCEQ action level of 500 mg/kg reduced by 20 percent margin of error to minimize the potential for contaminated areas to go undetected. The margin of error was selected based on recent experiences with field XRF analyses at other similar small arms ranges.

3. A comprehensive listing of the relevant, medium-specific, risk-based screening levels (RBSLs), potential chemical-specific Applicable or Relevant and Appropriate Requirements (ARARs) for the MC of concern (specifically antimony, arsenic, lead, copper, tin, zinc, and PAHs), and established background soil concentrations for the metals of concern. The RBSL and ARARs for this project are Texas Risk Reduction Program (TRRP) Protective Concentration Levels (PCLs). Texas-specific background concentrations [30 TAC 350.51(m)] will be used to determine background concentrations of metals in soil. The higher of the back ground concentration or PCL will be used. Laboratory Method Detection Limits (MDLs) for the proposed analytical methods should not exceed screening levels and ARARs. Practical quantitation limits should not exceed risk-based project action levels [Texas Risk Reduction Program (TRRP) Protective Concentration Levels (PCLs)]. The applicable numerical values can be found in Worksheet No. 15.

4. Analytical data characterizing MC concentrations in soil. Soil samples will be analyzed for MC metals using SW-846 Method 6010B and for PAHs using SW-846 Method 8270C in a fixed-base laboratory. Lead will also be analyzed in the field using a field portable XRF detector. MC concentrations in soil will be compared to site screening levels and/or background concentrations.

5. Laboratory analytical data characterizing soil pH, Total Organic Carbon (TOC), and Cation Exchange Capacity (CEC). These data are necessary for the evaluation of MC environmental fate and transport and will be obtained from fixed-base laboratory analyses.

6. Field identification/classification of soil types (i.e., lithology). Worksheet No. 21 contains relevant SOPs.

7. QA/QC specifications and the results of QA/QC reviews (e.g., data validation and usability assessment) conducted throughout the investigation. See specifications provided in Worksheet Nos 19 through 37.

DEFINE THE BOUNDARIES OF THE STUDY (STEP 4)

The current site investigation is limited to the evaluation of soil at the Skeet Range. An investigation of groundwater underlying the site is beyond the scope of this investigation but may be required based on the outcome of this investigation. A graphical illustration of the Skeet Range is provided as Figure 10.1.3 in Appendix A. The following items address the horizontal, vertical, and temporal boundaries for the study:

1. The populations of interest include soil that may have been contaminated directly by site operations or by subsequent migration of contaminants.

2. The initial horizontal study boundary will encompass the area that, based on historical information, is most likely impacted by site activities. Lateral expansion of this horizontal study boundary may be necessary if MC concentrations detected in the samples collected along this boundary exceed screening levels (see Step 5, Decision Rules). The study area has the following sub-zones: (1) an area downrange of the firing line where clay “target fragments” (i.e., fragments of targets actually hit by projectiles shotguns) would have accumulated (spent lead shot would also be present in this area); (2) an area

downrange of the target fragments where used/weathered targets not hit by projectiles from shotguns (i.e., missed targets) would have accumulated; (3) an area downrange of the firing line, target fragments, and used/weathered target fragments where the greatest concentrations of lead shot would have accumulated (targets and target fragments are unlikely to be in this area). The site may be further divided horizontally if analytical data suggest that "hot spot" zones are present at the site.

3. The initial vertical study boundary will be limited to 12 inches bgs because the CSM indicates that penetration of soil by MC is not generally expected to be deeper than this. However, the maximum investigation depth will not go beyond 5 feet bgs. The 5 foot depth corresponds to the TRRP residential definition of surface soil and is the practical depth limit for samples to be collected using a hand auger.

4. The temporal boundary is not a significant consideration in this study because MC concentrations (metals and PAHs) are anticipated to be relatively unchanged (stable) over the course of time needed to conduct the environmental investigations.

DEVELOP THE ANALYTICAL APPROACH (STEP 5)

Decision rules for this investigation include the following:

Risk Screening Decision Rules:

1. If MC concentrations in soil represent unacceptable human health risk, as determined by an evaluation of the representative soil concentrations in each individual sample result compared to the human health screening values, proceed to an RI (see step 2); otherwise, recommend NFA.

2. If MC concentrations in soil exceed human health screening values, additional risk evaluation will be conducted whereby the soil data will also be compared to the ecological screening values. This is possible because the laboratory quantitation limits are low enough to detect concentrations of MC in soil that may be harmful to ecological receptors. In this case the maximum detected MC concentrations in surface soil will be compared to screening concentrations to determine if a contaminant is a chemical of potential concern (COPC). If risks are determined to be "unacceptable" based on an evaluation of several lines of evidence (e.g., number of exceedances of screening criteria, magnitude of the exceedances of screening criteria,

spatial distribution of data, home range, background concentrations, etc.), the project team will determine the need to proceed with an RI or some type of remedial response action.

Protection of Groundwater Decision Rule:

1. If MC concentrations in any soil sample exceed background levels and/or TCEQ values for groundwater protection, recommend an evaluation of the need for an investigation of groundwater contamination. Otherwise, do not recommend a groundwater investigation be initiated on the basis of soil concentrations.

Delineation Decision Rules:

1. Horizontal Delineation: If the XRF-measured concentrations of lead in soil on the perimeter of the sample grid exceed 400 mg/kg, “step-out” if possible. Additional sample grids (approximately 150 ft by 150 ft) will be established and field XRF analysis of additional soil samples will continue until results of the XRF analysis are less than 400 mg/kg. The number of step-outs will be determined by the project team.

2. Vertical Delineation: If the XRF measured concentration of lead in soil exceeds 400 mg/kg, additional soil samples at depth will be collected. Soil samples will be collected at 2 foot increments up to 5 feet bgs for XRF lead analysis. The maximum sample depth is 5 ft bgs. The 5 foot depth corresponds to the TRRP residential definition of surface soil and is the practical depth limit for samples to be collected using a hand auger. XRF lead analysis of additional soil samples will continue until the results of the XRF analysis are less than 400 mg/kg or 5 feet bgs is reached.

3. If visible lead shot is concentrated in an area (based on field observations), a second sample from beneath the initial soil sample up to a maximum depth of 5 feet will be obtained (refer to Delineation Decision Rule #2).

4. If the analytical MC soil concentrations are less than screening values and/or background concentrations for metals, recommend NFA; otherwise, proceed to an RI.

SPECIFY PERFORMANCE OR ACCEPTANCE CRITERIA (STEP 6)

Both the XRF field screening samples and the laboratory soil samples locations were strategically selected to determine the extent of soil contamination throughout the intended study area and whether the soil contamination may present human health risks to site users. Understanding of the general layout of skeet ranges, areas most likely to be contaminated, the Conceptual Site Model, and information presented in the *Characterization and Remediation of Soils at Closed Small Arms Firing Ranges*, [Interstate Technology Regulatory Council (ITRC), January 2003] allowed for development of a conservative yet biased sampling approach. This biased selection of sample locations does not support the use of quantitative statistics to estimate decision performance as specified in the US EPA Guidance on Systematic Planning Using the Data Quality Objectives Process (EPA QA/G-4, 2006). Instead, the project team will use the results of the investigation to determine whether the amount and type of data collected is sufficient to support the attainment of project objectives. This will involve an evaluation of contaminant concentrations to ensure that contaminants are likely to have been detected if present, and that enough data have been collected to support delineation of contamination and a screening level human health risk assessment. The project team will review these assessments to ensure that all viewpoints are included in the assessment. Additionally, the Visual Sampling Plan (VSP) software tool was used to determine the minimum number of soil samples necessary assuming that lead was the primary contaminant of concern. A report produced by the VSP software version 4.6d is included as Appendix E. Based on the VSP output, the following key assumptions and performance/acceptance criteria were used to determine the number of soil samples:

- For purposes of statistical analysis, the “null hypothesis” is that the site was “dirty” (i.e., the mean lead concentration at the site exceeds the action level selected for statistical analysis).
- S (Sigma) = the estimated standard deviations for areas assumed to be relatively uncontaminated (clean), contaminated (dirty), and the transition zone were set at 100 mg/kg, 8,330 mg/kg, and 830 mg/kg, respectively.
- Delta = the width of the gray region, which was set equal to 150 mg/kg for clean areas, 14,600 mg/kg for contaminated areas, 1,600 mg/kg for the transition zone.
- Alpha = the tolerance for concluding that the site is “clean” when the site is actually “dirty”. If an incorrect decision was to be made, the team prefers to incorrectly take action to remediate a clean site rather than to fail to take action at a dirty site. Making an incorrect decision becomes less tolerable as the site becomes increasingly contaminated

or increasingly clean relative to the action level. Therefore, at a true mean concentration infinitesimally greater than the action level, the consequence of a decision error is not as great as, for example, if the true mean concentration was two times the action level. The tolerance for incorrectly concluding that the site mean is less than two times the action level when it is infinitesimally greater than the action level was set at 15 percent.

- Beta = the tolerance for concluding that the site is “dirty” when the site is actually “clean” was also established considering the tolerance for incorrectly concluding that the site mean is greater than the action level when it is actually infinitesimally less than 0.9 times the action level was set to 25 percent. This Beta value is greater than the Alpha value because there is more tolerance for this type of error than for the error of not taking action when a site is dirty.
- The lower bound of the grey region (LBGR) presented in terms of a percentage of the action level: 90 percent.
- The action levels selected for statistical analysis: The action levels are analyte specific as presented in Worksheet No. 15.

The results of the statistical analysis presented in Appendix E are that a minimum of five soil samples should be collected across each of the designated areas to be sampled and for which a decision must be made. The sampling design presented in Step 7 is based on this recommended number of samples, in addition to professional judgment and an understanding of the CSM, to determine the boundaries of contamination and areas that may require further investigation or some type of response action. A greater number of samples are planned for this investigation because delineation is a secondary study goal and it is cost effective to gather data when the field team is mobilized. Additionally, the field collected data will be used for correlation to laboratory data and as a result more than five samples must be collected. All new analytical data collected per the Step 7 sampling design should meet the QA criteria established in Worksheets 19 through 37 and the prescribed detection limit requirements for the MC constituents of concern.

DEVELOP THE PLAN FOR OBTAINING DATA (STEP 7)

The proposed SI field data collection program for the Skeet Range is presented, to a large extent, on Figure 17-1. The information developed in DQO Steps 1 through 6 was used to develop the program, which assumes that the majority of contamination is present in the 0-to 12-inch bgs soil interval. As noted above, the program also assumes, based on the CSM, that the following potential depositional areas exist downrange of the firing line:

- An area where clay "target fragments" (i.e., fragments of targets actually hit by shotguns) would have accumulated (spent lead shot would also be present in this area).

- An area where used/weathered targets not hit by shotgun shells (i.e., missed targets) would have accumulated.

- An area where the greatest concentrations of lead shot would accumulate (targets and target fragments are unlikely to be within this area).

The zone of maximum shot accumulation for the Skeet Range is presumed to occur down range 770 feet (based on *Characterization and Remediation of Soils at Closed Small Arms Firing Ranges. January 2003. Interstate Technology Regulatory Council*).

As noted in Step 4, the horizontal and vertical boundaries of the soil areas to be sampled will encompass all areas significantly impacted by site activities.

The sampling design consists of samples in a grid pattern extending from the shooters' positions to the maximum shot fall line to ensure that the decision units are well represented spatially. The MC sampling and analytical program for soil samples is as follows:

- Soil
    - Surface soil samples (0 to 12 inches bgs) will be screened via the field portable XRF in the area to be sampled as shown on Figure 17-1. Additionally, a site "walk over" will be conducted by the FOL to identify any obvious areas of fragment/lead shot accumulation. Up to 10 additional "discretionary" surface soil samples may be collected based on visual observation of accumulated fragments or shot in the area to be sampled. Emphasis will be placed on collecting samples required to delineate contaminated areas. Additional horizontal "step-out" samples will also be collected at the boundaries of the area to be sampled if XRF lead concentrations are greater than 400 mg/kg in the initial surface soil samples.

    - Vertical step out XRF samples (starting at 1 foot bgs) may also be collected if the corresponding surface soil sample lead concentration exceeds 400 mg/kg. If the step-out XRF lead concentration also exceeds 400 mg/kg, additional subsurface

soil samples will then be collected vertically up to a maximum depth of 5 feet, depending on soil conditions, until lead concentrations in subsurface soil do not exceed 400 mg/kg or until collection of samples via a hand auger becomes impractical.

- Analytical Program

  All soil samples will be analyzed for lead using XRF field screening analysis. A correlation analysis (field screening versus fixed-base laboratory concentrations) will conducted to support data interpretation for the investigation. This analysis will determine the linear correlation between field and laboratory data. The correlation coefficient shall be greater than or equal to 0.65 and less than or equal to 1.00. Correlation analyses will not be generated for the five other metals.

  - Eighteen soil samples (one from each sample grid) will be analyzed for MC metals of concern at a fixed-base laboratory.

  - Eighteen soil samples (one from each sample grid) will be analyzed for PAHs at a fixed-base laboratory.

  - Up to 10 discretionary soil samples collected in the downrange area potentially contaminated with spent targets and target fragments and lead shot will also be analyzed for metals of concern and/or PAHs.

  - Up to 3 soil samples will be analyzed for pH, CEC and TOC.

Data users and other plan specifications are provided throughout the remainder of this SAP.

SAP Worksheet No. 12 -- Measurement Performance Criteria Table Field Quality Control Sample – All Analyses, All Matrices

(UFP-QAPP Manual Section 2.6.2)

QC Sample	Analytical Group	Frequency	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
Equipment Rinsate Blank	All Fractions	One per 20 field samples per matrix per type of reusable sampling equipment	Bias/Contamination	Detections ≤ QL	S&A
Field Duplicate	All Fractions	One per 10 field samples collected	Precision	Aqueous samples Relative Percent Difference (RPD) of ≤30; Solid samples RPD of ≤50	S
Cooler Temperature Blank	All Fractions	One per cooler	Accuracy/ Representativeness	Between 2 and 6° C	S

1) Field quality control samples will not be collected for miscellaneous parameters (i.e., pH, Total Organic Carbon, Cation Exchange Capacity) or waste disposal parameters (i.e., Toxicity Characteristic Leaching Procedure (TCLP) metals, Reactivity, Corrosivity, and Ignitability [RCI], or total petroleum hydrocarbons [TPH] analyses).

SAP Worksheet No. 13 -- Secondary Data Criteria and Limitations Table

(UFP-QAPP Manual Section 2.7)

Secondary Data	**Data Source** (originating organization, report title and date)	**Data Generator(s)** (originating organization, data types, data generation / collection dates)	**How Data Will Be Used**	**Limitations on Data Use**
Site Histories, Initial CSM	Preliminary Assessment, Naval Auxiliary Landing Field Waldron, Texas, April 2005	Malcolm Pirnie, Inc	Basis for UFP QAPP, Site Histories, and CSMs	The information is qualitative, and no quantitative (site-specific nature and extent of contamination) information is available. The information was used to establish the field work program and identify areas most likely to be contaminated.

This is the initial phase of field investigation at the Skeet Range, and no known secondary data exists.

SAP Worksheet #14 -- Summary of Project Tasks

(UFP-QAPP Manual Section 2.8.1)

The Skeet Range SI project activities consist of the following tasks:

- Field tasks, including:
  - Mobilization/demobilization and Utility Clearance
  - Drilling and soil sample collection
  - Quality control samples
  - Field Instrument calibration
  - Decontamination
  - IDW removal and disposal
  - Global Positioning System
  - XRF lead analysis of soil
- Analytical Tasks
- Data Management
- Assessment and Oversight
- Data Review
- Project Report

These tasks are summarized below. The standard operating procedures (SOPs) and field documents referenced below and in other worksheets are included in Appendices B and D, respectively.

Field Tasks

- **Mobilization/Demobilization:** Mobilization/demobilization activities include: field equipment procurement and transport to the work site, subcontractor procurement and coordination, utility awareness and clearance, location and setup of areas for decontamination and waste storage, acquisition of vehicles, and establishment of an on-site staging area.

  Equipment requirements will be finalized by the FOL following acceptance of the UFP SAP. The FOL will review the scope of work and assemble equipment (e.g., vehicles and sampling, personal protective equipment [PPE], and decontamination equipment) to implement and complete the field investigations.

This list will be reviewed by the project team and the PM. The FOL will be responsible for receiving and unpacking the equipment and ensuring that all equipment is operable and calibrated.

The FOL will be responsible for tracking equipment used in the field. Analytical laboratory services have been subcontracted and the FOL will be responsible for coordinating associated field activities. The Tetra Tech FOL will be responsible for coordinating the analytical services, and the acquisition and delivery of sample containers to the site.

During mobilization, the FOL will review the roles and responsibilities of each field team member and review the requirements of the various field activities. A series of meetings will be conducted to review the sampling and analytical requirements. Upon mobilization, an on-site meeting will be conducted to review health and safety requirements. The Site Safety Officer (SSO) will be responsible for reviewing the HASP with the field team members and subcontractors.

- **Utility Clearance Tasks:** Prior to commencing any work at NALF Cabaniss, NASCC personnel will be contacted, and a review of utility and operational subsurface features will be conducted. The proposed areas of intrusive activities will be noted on a facility map and field located for clearance by NASCC personnel. Texas One Call will also be notified for subsurface utility clearance, in accordance with state law. Work permits, if required by the facility, will be obtained prior to conducting field activities. The FOL will be responsible for coordinating these activities.

- **Drilling Tasks:** All soil borings at the sket range will be advanced utilizing hand augering techniques in accordance with SOP-05 (Soil Coring and Sampling Using Hand Augering Techniques). All borings will be logged in accordance with SOP-10 (Borehole and Soil Sample Logging). Methods for recording data are included in each SOP. Field SOPs are included in Appendix A.

- **Sample Collection Tasks:** Surface and subsurface soil samples will be collected in accordance with SOP-05 (Soil Coring and Sampling Using Hand Augering Techniques) and SOP-06 (Borehole Advancement and Soil Coring and Sampling Using Direct-Push Technology). The sample numbering scheme will be in accordance with SOP-02 (Sample Identification and Nomenclature). Methods for recording data are included in each SOP and SOP-03 (Sample Custody and Documentation of Field Activities). Sample labeling will be in

accordance with SOP-01 (Labeling), and sample containers, preservation, packaging, and shipping will be in accordance with SOP-11 (Sample Packaging). Field SOPs are included in Appendix B of this document.

Surface soil samples (considered to be within 0 to 1 feet bgs) will be collected using a hand auger, hand trowel, or disposal sampler. All soil from the ground surface to depth will be a composite of one sample over the sample's depth interval. The sample will be composited in one container. The numbers and types of samples to be collected along with associated analyses to be conducted are presented in Worksheet No. 18.

The numbers and types of samples to be collected at each site along with associated analytical programs are presented in Tables 18.1 through 18.5.

- **Quality Control Tasks:** Equipment blanks, field duplicates, matrix spikes, and matrix spike duplicates will be collected as presented in Worksheet No. 20.

  Initial and continuing calibrations, tuning, reagent blanks, surrogates, duplicates, laboratory control samples, and all other applicable QC for all analytical methods is presented in Worksheet No. 22.

- **Field Instrument Calibration:** These procedures are described in Worksheet No. 22.

- **Equipment Decontamination**: All reusable sampling equipment (e.g., stainless steel trowels, etc.) will be decontaminated prior to sampling and between samples, according to the sequence established in SOP-04 (Appendix B).

- **Investigation-Derived Waste Tasks:** It is anticipated that waste materials will be generated during the field investigation. Investigative-derived waste (IDW) generated during the SI will be stored on site and will remain there until waste characterization results are available and disposal is implemented. Drums of IDW will be stored at NALF Waldron at a location designated by the Navy.

  Waste profiling will be completed as follows:

- Liquids - One aliquot will be collected from each drum of IDW liquids and composited into one liquid sample. The liquid sample will be analyzed for Toxicity Characteristic Leaching Procedure (TCLP) metals, TCLP volatile organic compounds (VOCs), reactivity, corrosivity, and ignitability (RCI), and total petroleum hydrocarbons (TPH).

- Soil - One aliquot will be collected from each drum of IDW soil and composited into one soil sample. The soil sample will be analyzed for TCLP metals, TCLP VOCs, RCI and TPH.

Upon completion of waste profiling activities, the results will be transmitted to NASCC personnel who will be responsible for the manifesting and disposal of the IDW. SOP-09 located in Appendix A provides information on the handling of investigation-derived waste.

- **Global Positioning System (GPS):** A GPS survey will be used to locate all sampling points.

- **XRF Analysis:** On-site field XRF analysis for lead will be conducted. Each soil sample collected will be field screened using a portable field XRF unit. XRF field screening will be conducted in accordance with SOP-14 (Use of Field Portable X-Ray Fluorescence Analysis of Soil and Sediment), and XRF results will be recorded on sample log sheets.

Analytical Tasks - Chemical analysis for Select Metals (antimony, arsenic, copper, lead, tin, and zinc) and PAHs will be performed by the subcontracted laboratory, Empirical Laboratories of Nashville, Tennessee. Empirical Laboratories is NFESC approved and NELAP accredited. Analyses will be performed in accordance with the analytical methods identified in Worksheet #30. Empirical Laboratories will meet the PQLs specified in Worksheet No. 15. Empirical Laboratories will perform the chemical analyses following laboratory-specific SOPs (Worksheet Nos. 19 and 23) developed based on the methods listed in Worksheet Nos. 19 and 30. Copies of the laboratory SOPs are included in Appendix C on the attached CD. TestAmerica will perform the solid and aqueous IDW analysis using Method TPH TX 1005.

Data Management

- Project documentation and records

- Field sample collection and field measurement records are described in Worksheet Nos. 27 and 29.
- Laboratory data package deliverables are described in the analytical specifications.
- Data assessment documents and records are listed in Worksheet No. 29.

- Data recording formats are described in Worksheet No. 27.

Data Handling and Management - After the field investigation is completed, the field sampling log sheets will be organized by date and media and filed in the project files. The field logbooks for this project will be used only for this Site, and will also be categorized and maintained in the project files after the completion of the field program. Project personnel completing concurrent field sampling activities may maintain multiple field logbooks. When possible, logbooks will be segregated by sampling activity. The field logbooks will be titled based on date and activity. The data handling procedures to be followed by the laboratories will meet the requirements of the technical specification. The electronic data results will be automatically downloaded into the Tetra Tech database in accordance with proprietary Tetra Tech processes.

Data Tracking and Control. The Tetra Tech PM (or designee) is responsible for the overall tracking and control of data generated for the project.

- **Data Tracking**. Data is tracked from its generation to its archiving in the Tetra Tech project-specific files. The Tetra Tech Project Chemist (or designee) is responsible for tracking the samples collected and shipped to the contract laboratory. Upon receipt of the data packages from the analytical laboratory, the Project Chemist will oversee the data validation effort, which includes verifying that the data packages are complete and results for all samples have been delivered by the analytical laboratory.

- **Data Storage, Archiving, and Retrieval**. The data packages received from the subcontract laboratory are tracked in the data validation log book. After the data are validated, the data packages are entered into the Tetra Tech CLEAN file system and archived in secure files. The field records including field log books, sample logs, chain-of-custody records, and field calibration logs will be submitted by the FOL to be entered into the CLEAN file system prior to archiving in secure project files. The project files are audited for accuracy and completeness. At the completion of the Navy contract the records will be stored by Tetra Tech.

- **Data Security**. The Tetra Tech project files are restricted to designated personnel only. Records can only be borrowed temporarily from the project file using a sign-out system. The Tetra Tech Data Manager maintains the electronic data files. Access to the data files is restricted to qualified personnel only. File and data backup procedures are routinely performed.

Assessment and Oversight – Refer to Worksheet No. 32 for assessment findings and corrective actions and Worksheet No. 33 for QA management reports.

Data Review

- Data verification is described in Worksheet No 34.
- Data validation is described in Worksheet Nos. 35 and 36.
- Usability assessment is described in Worksheet No. 37.

Project Report - Draft and Final versions of project reports will be prepared and submitted to the Navy, EPA, and TCEQ for review. The reports will include the following sections:

- Executive Summary – a very brief description of the work conducted and the findings.

- Introduction and Background – includes a description of the history of operations and activities at the Site and a summary of any previous investigations and removal actions.

- Description of Field Investigations – includes a summary of the work performed in the approved SAP and any field modifications as documented by the FOL. This section will include maps showing the sampling locations and tables summarizing the data collected.

- Data quality – includes a summary of quantitative analytical performance indicators such as completeness, precision, bias and sensitivity, as well as qualitative indicators such as representativeness and comparability. Includes a reconciliation of project data with the DQOs and an identification of deviations from this SAP.

  A data usability assessment will be used to identify significant deviations in analytical performance that could affect the ability to meet project objectives. The elements of this review are presented in Worksheet No. 37.

- Nature and Extent of Contamination – includes the contamination previously found in each medium sampled in relation to the conceptual model of the site. This section will note the removals previously conducted, the contamination addressed and any additional contaminants found during this effort. Detected contaminant concentrations will be tabulated for each medium and depicted on maps.

- Contaminant Fate and Transport – includes a description of the contaminants detected and their behavior in the soil and bedrock, particularly with emphasis on the future migration of these contaminants to any possible exposure areas.

- Summary and Conclusions – this section will summarize the findings, conclude whether delineation of contamination is adequate, and recommend further sampling if needed.

Tetra Tech will respond to comments received on the draft report. Tetra Tech will submit the draft report before any additional sampling begins. The final version of the report will submitted in hardcopy and electronic format to the project stakeholders.

SAP Worksheet No.15 -- Reference Limits and Evaluation Table

(UFP-QAPP Manual Section 2.8.1)

Matrix: Soil

Analytical Group: Inorganics, PAHs

Analyte	CAS Number	Project Action Limit[1] (mg/kg)	Project Action Limit Reference	Project Quantitation Limit Goal (mg/kg)	Empirical Laboratory[2]	
					Quantitation Limit (mg/kg)	Method Detection Limit (mg/kg)
Inorganics						
Antimony	7440-36-0	15	TRRP Soil PCL	3.0	3.0	1.0
Arsenic	7440-38-2	24	TRRP Soil PCL	1.0	1.0	0.6
Copper	7440-50-8	550	TRRP Soil PCL	2.0	2.0	1.0
Lead	7439-92-1	500	TRRP Soil PCL	0.60	0.60	0.30
Tin	7439-92-1	35,000	TRRP Soil PCL	5.0	5.0	1.0
Zinc	7440-06-66	9900	TRRP Soil PCL	4.0	4.0	1.0
PAHs 8270C						
1-Methylnaphthalene	90-12-0	150	TRRP Soil PCL	0.0033	0.0033	0.0013
2-Methylnaphthalene	91-57-6	250	TRRP Soil PCL	0.0033	0.0033	0.0013
Acenaphthene	83-32-9	3000	TRRP Soil PCL	0.0033	0.0033	0.0011
Acenaphthylene	208-96-8	3800	TRRP Soil PCL	0.0033	0.0033	0.00095

Analyte	CAS Number	Project Action Limit[1] (mg/kg)	Project Action Limit Reference	Project Quantitation Limit Goal (mg/kg)	Empirical Laboratory[2]	
					Quantitation Limit (mg/kg)	Method Detection Limit (mg/kg)
Anthracene	12-01-27	18,000	TRRP Soil PCL	0.0033	0.0033	0.0011
Benzo(a)anthracene	56-55-3	5.7	TRRP Soil PCL	0.0033	0.0033	0.00085
Benzo(a)pyrene	50-32-8	0.56	TRRP Soil PCL	0.0033	0.0033	0.00085
Benzo(b)fluoranthene	205-99-2	5.7	TRRP Soil PCL	0.0033	0.0033	0.00065
Benzo(g,h,i)perylene	191-24-2	1800	TRRP Soil PCL	0.0033	0.0033	0.00040
Benzo(k)fluoranthene	207-08-9	57	TRRP Soil PCL	0.0033	0.0033	0.00075
Chrysene	218-01-9	560	TRRP Soil PCL	0.0033	0.0033	0.00047
Dibenzo(a,h)anthracene	53-70-3	0.55	TRRP Soil PCL	0.0033	0.0033	0.00034
Fluoranthene	206-44-0	2300	TRRP Soil PCL	0.0033	0.0033	0.00070
Flourene	86-73-7	2300	TRRP Soil PCL	0.0033	0.0033	0.00095
Indeno(1,2,3-cd)pyrene	193-39-5	5.7	TRRP Soil PCL	0.0033	0.0033	0.00080
Naphthalene	91-20-3	220	TRRP Soil PCL	0.0033	0.0033	0.0013
Phenanthrene	85-01-8	1700	TRRP Soil PCL	0.0033	0.0033	0.00085
Pyrene	129-00-0	1700	TRRP Soil PCL	0.0033	0.0033	0.00065

Matrix: Soil

Analytical Group: Inorganics - Lead (Field Data collected via Field Portable X-Ray Fluorescence (FPXRF) Analyzer)

Analyte	CAS Number	Project Action Limit[1] (mg/kg)	Project Action Limit Reference	Project Quantitation Limit Goal (mg/kg)	Method Detection Limit (mg/kg)
Lead	7439-92-1	400	TRRP Soil PCL	10	10[3]

Lead is the primary contaminant from operations at small arms and skeet ranges. Other metals (antimony, arsenic, copper tin, zinc) and PAHs are expected to be associated with lead. Field XRF will be used to analyze samples for lead to delineate clean and contaminated locations. Samples from both clean and contaminated locations will be sent to a fixed-base laboratory for analysis. Therefore, the use of field XRF to meet the Project Action Limit is acceptable because all decisions will be based on fixed-base laboratory data, which will meet the Project Action Limits.

Matrix: Leachate

Analytical Group: TCLP Regulatory List

Analyte	CAS Number	Project Action Limit (mg/L)	Project Action Limit Reference	Project Quantitation Limit Goal (mg/L)	Empirical Laboratory[2]	
					Quantitation Limit (mg/L)	Method Detection Limit (mg/L)
Benzene	71-43-2	0.5	USEPA	0.16	0.001	0.0004
Carbon tetrachloride	56-23-5	0.5	USEPA	0.16	0.001	0.0002
Chlorobenzene	108-90-7	100	USEPA	33	0.005	0.002
Chloroform	67-66-3	6	USEPA	2	0.002	0.0005
1,2-dichloroethane	107-06-2	0.5	USEPA	0.16	0.001	0.0004
1,1-dichloroethene	75-35-4	0.7	USEPA	0.23	0.001	0.0004
2-butanone	78-93-3	200	USEPA	66	0.0012	0.004
Tetrachloroethene	127-18-4	0.7	USEPA	0.23	0.001	0.0002
Trichloroethene	79-01-6	0.5	USEPA	0.16	0.001	0.0005
Vinyl chloride	75-01-4	0.2	USEPA	0.06	0.001	0.0004
Arsenic	7440-38-2	5	USEPA	1.6	0.005	0.003
Barium	7440-39-3	100	USEPA	33	0.004	0.005
Cadmium	7440-43-9	1	USEPA	0.33	0.005	0.001
Chromium	7440-47-3	5	USEPA	1.6	0.005	0.002
Lead	7439-92-1	5	USEPA	1.6	0.003	0.0015
Mercury	7439-97-6	0.2	USEPA	0.06	0.0002	0.00008
Selenium	7782-49-2	1	USEPA	0.33	0.005	0.003
Silver	7440-22-4	5	USEPA	1.6	0.002	0.001

Notes: TOC, CEC, and pH are not included here as these analyses are being conducted to provide fate and transport information.

Abbreviations:

CAS = Chemical Abstracts Service
MDL = Method Detection Limit
mg/kg = milligrams per kilograms
mg/L = milligrams per liter
PCL = Protective Concentration Level
QL = Quantitation Limit
TRRP = Texas Risk Reduction Program

Footnotes:

1 Project Action Limits are from TRRP Table 1, Tier 1 Residential Soil PCLs for total soil combined pathway, March 25, 2009.
2 The Laboratory QLs and MDLs for Empirical Laboratory are presented.
3 USEPA. EPA/540/R-06/002. February 2006. Value from EPA study of manufacturers equipment.

SAP Worksheet No. 17 -- Sampling Design and Rationale

(UFP-QAPP Manual Section 3.1.1)

SAMPLING LOCATIONS, ANALYSES, AND RATIONALES

This section identifies sampling locations, QA/QC samples to be collected, analyses to be performed, and rationales for the sampling and analytical program. The samples collected from the surface soil interval (0 to 12 inches bgs) will be prepared and analyzed according to the normal laboratory protocol as identified in Worksheet No. 30. Sampling locations are shown on Figure 17-1.

Although MEC is not expected within the investigation site, if MEC are observed in or around any work area, work must be halted. The presence of MEC must be communicated to the FOL, and the FOL will then communicate with NASCC personnel so that appropriate action may be taken. If obvious soil staining is observed in any sample location, the staining will be described in the sample log sheet, and additional samples may be collected at the discretion of the FOL or site geologist to determine the nature and possibly the extent of associated site-related contamination.

The total numbers of soil analyses for each analyte group are shown in Worksheet Nos. 18 and 20. Soil QA/QC samples will be collected at frequencies listed in Worksheet No. 20. Worksheet No. 19 presents a summary of the sample analyses, container types and volumes, preservation requirements, and holding times for the samples to be collected.

Soil Sampling Strategy

The chosen sampling strategy employs a judgmental design and grid to target those areas that are most likely to be contaminated according to the CSM presented in Appendix A. This is a conservative strategy, and the data collected under this strategy will probably not represent the concentrations to which human or ecological receptors would actually be exposed. Instead, the measured concentrations are likely to be greater than actual exposure concentrations. The strategy therefore ensures that a potential environmental problem is not overlooked. The sampler will try to ensure good spatial coverage of the targeted contamination areas when selecting sampling locations to validate the sampling design and CSM; areas outside of those expected to be contaminated will also be sampled. If the CSM is correct, these locations will exhibit significantly lesser, and perhaps even non-detectable, concentrations of MC than are found in the

targeted contamination areas. Surface soil sampling will be performed using a hand auger, hand trowel, or disposal sampler. The soil borings will be logged in the field notebook or sample log sheets to determine lithology. Details regarding soil sampling equipment and procedures are included in Worksheet No. 14 and SOP-05.

The soil borings will initially be advanced to a maximum depth of 12 inches bgs, and one soil sample will be collected from each boring and analyzed for lead in the field using XRF equipment in accordance with SOP-14. The sample will consist of soil from the entire 0- to 12-inch depth interval.

Based on any initial XRF measurements exceeding 400 mg/kg, the FOL will use the delineation decision rules (worksheet #11m Step 5) in determining the need to collect an additional sample at a greater depth or if it is necessary to “step out” to determine the extent of contamination at that particular location. Care will be taken to mix samples in a plastic bag before field XRF measurement. Three separate XRF measurements will be made for each sample, and care will be taken to mix the sample in the plastic bag between measurements. The average of the three readings will be computed and recorded as the concentration value for the sample.

Actual sample locations may vary from the proposed locations based on field conditions observed during an initial site walkover by the FOL provided that locations remain in the estimated range area as depicted on Figure 17-1. The FOL will use his professional judgment and inspection of the site to determine which areas are most likely to be contaminated and bias the sampling towards those areas. The professional judgment will take into account the topography of the site and the FOL’s understanding of site operations. Global Positioning System (GPS) measurements will be taken at each individual sample location, which will allow for future repeatable investigations or guide in any remedial action. During the processing of samples for XRF field analysis, any observed lead bullets, bullet fragments, or lead shot will be removed from the sample so as not to bias the sample with high metals result. The sampling objective is to determine the metals concentrations in soil as a result of potential leaching of contaminants from the bullets. However, the presence of bullets, bullet fragments, or lead will be described in the individual field sample log sheets (see SOP-03) and will also be used as the basis for collection of “step-out” samples (horizontal or vertical) even if the XRF results are less than the 400 mg/kg threshold. The visual observations will be noted on the soil sample log. All bullets, bullet fragments, or lead shot removed from any sample will be placed in a plastic bag, labeled with the sample number and submitted to the laboratory along with the associated samples. The

laboratory will weigh the sample and report the weight along with the analytical results. The reported weights of removed materials will be used to calculate total concentrations if the mass of removed material was to degrade in the future.

The field XRF and laboratory data for metals and PAHs are intended to be used to establish the nature and extent of contamination and potential environmental mobility. Soil properties (pH, TOC, and CEC) are principal determinants of environmental mobility; therefore, selected samples (up to three) will be analyzed for these parameters.

Lead is the major contaminant of concern at the Skeet Range site. The other contaminants (arsenic, antimony, tin, copper, zinc. and PAHs) are expected to be associated with lead. Field XRF data for lead will be used as the indication of potential contaminations. Fixed-base-laboratory data will be used to establish a correlation between field XRF results for lead and laboratory data.

Skeet Range

The sampling design consists of samples in a grid pattern extending from the shooters' positions to the maximum shot fall line to ensure that the decision units are well represented spatially as shown on Figure 17-1. The MC sampling and analytical program for soil samples is as follows:

- Soil
    - Surface soil samples (0 to 12 inches bgs) will be screened via the field portable XRF in the area to be sampled as shown on Figure 17-1. Additionally, a site "walk over" will be conducted by the FOL to identify any obvious areas of fragment/lead shot accumulation. Up to 10 additional "discretionary" surface soil samples may be collected based on visual observation of accumulated fragments or shot in the area to be sampled. Emphasis will be placed on collecting samples required to delineate contaminated areas.

    - Vertical step out XRF samples (starting at 1 foot bgs) may also be collected if the corresponding surface soil sample lead concentration exceeds 400 mg/kg. If the step-out XRF lead concentration also exceeds 400 mg/kg, additional subsurface soil samples will then be collected vertically up to a maximum depth of 5 feet, depending on soil conditions, until lead concentrations in subsurface soil do not

exceed 400 mg/kg or until collection of samples via a hand auger becomes impractical.

- Analytical Program

  All soil samples will be analyzed for lead using XRF field screening analysis.

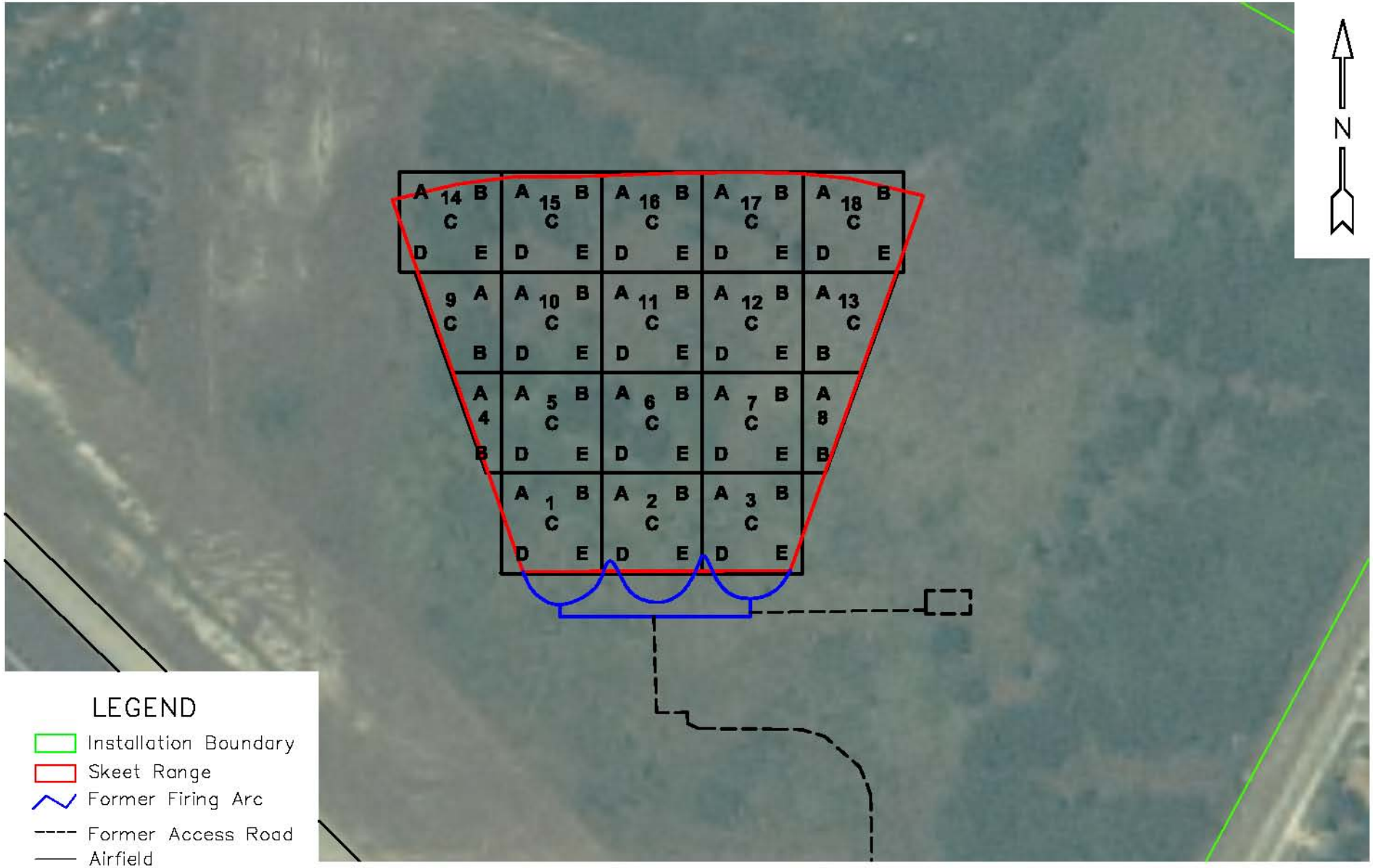
  - Eighteen soil samples (one from each sample grid) will be analyzed for MC metals of concern at a fixed-base laboratory.

  - Eighteen soil samples (one from each sample grid) will be analyzed for PAHs at a fixed-base laboratory.

  - Up to 10 discretionary soil samples collected in the downrange area potentially contaminated with spent targets and target fragments and lead shot will also be analyzed for metals of concern and/or PAHs.

  - Up to 3 soil samples will be analyzed for pH, CEC and TOC.

1514.dwg 08-20-08 gs



LEGEND

- Installation Boundary
- Skeet Range
- Former Firing Arc
- Former Access Road
- Airfield

0 200
Scale in Feet

DRAWN BY GS	DATE 10/29/08	SAMPLE LOCATIONS SKEET RANGE NALF WALDRON CORPUS CHRISTI, TEXAS	CONTRACT NO. 1514
CHECKED BY LB	DATE 8/20/08		OWNER NO. 0023
REVISED BY	DATE		APPROVED BY / DATE
SCALE AS NOTED			DRAWING NO. FIGURE 17-1 / REV. 0

NAVFAC

SAP Worksheet No. 18 -- Sampling Locations and Methods/SOP Requirements Table

(UFP-QAPP Manual Section 3.1.1)

SKEET RANGE

Grid Number	Subsample Identification	Composite Sample Identification[1]	Depth[2] (feet bgs)	Metals		pH	TOC	CEC	Semivolatile Organic Compounds
				Field XRF (Lead Only)	SW-846 3050B/6010B (lead, arsenic, antimony, tin, zinc, and copper)	Method SW-846 9045C	Method Lloyd Kahn	Method SW-846 9081	SW-846 8270C (PAH)
SOIL									
1	SR-SS01a	SR-SS01	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
1	SR-SS01b		0 – 1.0	X					
1	SR-SS01c		0 – 1.0	X					
1	SR-SS01d		0 – 1.0	X					
1	SR-SS01e		0 – 1.0	X					
2	SR-SS02a	SR-SS02	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
2	SR-SS02b		0 – 1.0	X					
2	SR-SS02c		0 – 1.0	X					
2	SR-SS02d		0 – 1.0	X					
2	SR-SS02e		0 – 1.0	X					
3	SR-SS03a	SR-SS03	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
3	SR-SS03b		0 – 1.0	X					
3	SR-SS03c		0 – 1.0	X					

Grid Number	Subsample Identification	Composite Sample Identification[1]	Depth[2] (feet bgs)	Metals		pH	TOC	CEC	Semivolatile Organic Compounds
				Field XRF (Lead Only)	SW-846 3050B/6010B (lead, arsenic, antimony, tin, zinc, and copper)	Method SW-846 9045C	Method Lloyd Kahn	Method SW-846 9081	SW-846 8270C (PAH)
3	SR-SS03d	SR-SS03	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
3	SR-SS03e		0 – 1.0	X					
4	SR-SS04a	SR-SS04	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
4	SR-SS04b		0 – 1.0	X					
5	SR-SS05a	SR-SS05	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
5	SR-SS05b		0 – 1.0	X					
5	SR-SS05c		0 – 1.0	X					
5	SR-SS05d		0 – 1.0	X					
5	SR-SS05e		0 – 1.0	X					
6	SR-SS06a	SR-SS06	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
6	SR-SS06b		0 – 1.0	X					
6	SR-SS06c		0 – 1.0	X					
6	SR-SS06d		0 – 1.0	X					
6	SR-SS06e		0 – 1.0	X					
7	SR-SS07a	SR-SS07	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
7	SR-SS07b		0 – 1.0	X					
7	SR-SS07c		0 – 1.0	X					
7	SR-SS07d		0 – 1.0	X					
7	SR-SS07e		0 – 1.0	X					

Grid Number	Subsample Identification	Composite Sample Identification[1]	Depth[2] (feet bgs)	Metals		pH	TOC	CEC	Semivolatile Organic Compounds
				Field XRF (Lead Only)	SW-846 3050B/6010B (lead, arsenic, antimony, tin, zinc, and copper)	Method SW-846 9045C	Method Lloyd Kahn	Method SW-846 9081	SW-846 8270C (PAH)
8	SR-SS08a	SR-SS08	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
8	SR-SS08b	SR-SS08	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
9	SR-SS09a	SR-SS09	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
9	SR-SS09b		0 – 1.0	X					
9	SR-SS09c		0 – 1.0	X					
10	SR-SS10a	SR-SS10	0 – 1.0	X	X	TBD[3]	TBD[(3)]	TBD[(3)]	X
10	SR-SS10b		0 – 1.0	X					
10	SR-SS10c		0 – 1.0	X					
10	SR-SS10d		0 – 1.0	X					
10	SR-SS10e		0 – 1.0	X					
11	SR-SS11a	SR-SS11	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
11	SR-SS11b		0 – 1.0	X					
11	SR-SS11c		0 – 1.0	X					
11	SR-SS11d		0 – 1.0	X					
11	SR-SS11e		0 – 1.0	X					
12	SR-SS12a	SR-SS12	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
12	SR-SS12b		0 – 1.0	X					
12	SR-SS12c		0 – 1.0	X					
12	SR-SS12d		0 – 1.0	X					

Grid Number	Subsample Identification	Composite Sample Identification[1]	Depth[2] (feet bgs)	Metals		pH	TOC	CEC	Semivolatile Organic Compounds
				Field XRF (Lead Only)	SW-846 3050B/6010B (lead, arsenic, antimony, tin, zinc, and copper)	Method SW-846 9045C	Method Lloyd Kahn	Method SW-846 9081	SW-846 8270C (PAH)
12	SR-SS12e		0 – 1.0	X					
13	SR-SS13a	SR-SS13	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
13	SR-SS13b		0 – 1.0	X					
13	SR-SS13c		0 – 1.0	X					
14	SR-SS14a	SR-SS14	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
14	SR-SS14b		0 – 1.0	X					
14	SR-SS14c		0 – 1.0	X					
14	SR-SS14d		0 – 1.0	X					
14	SR-SS14e		0 – 1.0	X					
15	SR-SS15a	SR-SS15	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
15	SR-SS15b		0 – 1.0	X					
15	SR-SS15c		0 – 1.0	X					
15	SR-SS15d		0 – 1.0	X					
15	SR-SS15e		0 – 1.0	X					
16	SR-SS16a	SR-SS16	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
16	SR-SS16b		0 – 1.0	X					
16	SR-SS16c		0 – 1.0	X					
16	SR-SS16d		0 – 1.0	X					
16	SR-SS16e		0 – 1.0	X					

Grid Number	Subsample Identification	Composite Sample Identification[1]	Depth[2] (feet bgs)	Metals		pH	TOC	CEC	Semivolatile Organic Compounds
				Field XRF (Lead Only)	SW-846 3050B/6010B (lead, arsenic, antimony, tin, zinc, and copper)	Method SW-846 9045C	Method Lloyd Kahn	Method SW-846 9081	SW-846 8270C (PAH)
17	SR-SS17a	SR-SS17	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
17	SR-SS17b		0 – 1.0	X					
17	SR-SS17c		0 – 1.0	X					
17	SR-SS17d		0 – 1.0	X					
17	SR-SS17e		0 – 1.0	X					
18	SR-SS18a	SR-SS18	0 – 1.0	X	X	TBD[3]	TBD[3]	TBD[3]	X
18	SR-SS18b		0 – 1.0	X					
18	SR-SS18c		0 – 1.0	X					
18	SR-SS18d		0 – 1.0	X					
18	SR-SS18e		0 – 1.0	X					

PAH = Polynuclear aromatic hydrocarbon
TOC = Total Organic Carbon
CEC = Cation Exchange Capacity
XRF = X-ray Fluorescence

1 Surface soil samples will be will be collected over a grid interval focused on the expected fallout-area. Proposed sample locations are shown on Figure 17-1.
2 Sample depth to a maximum of 12 inches below surface for soils. All samples will be collected in accordance with the respective SOP (Soil SOP-05).
3 At the discretion of the FOL, three additional soil samples will be collected for pH, TOC, and CEC analyses.

Note: Two duplicates and one MS/MSD samples will be collected.

SAP Worksheet No. 19 -- Analytical SOP Requirements Table
(UFP-QAPP Manual Section 3.1.1)

Matrix	Analytical Group	Analytical and Preparation Method/SOP Reference[1]	Containers (number, size, and type)	Sample volume[2] (units)	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time[3] (preparation / analysis)
Aqueous Field Quality Control	PAHs	SW-846 3510C/8270C, SOP-300/231	Two 1-liter glass amber bottles	1,000 milliliters	Cool to 4° C	7 days until extraction/40 days to analysis
Soil	PAHs	SW-846 3541/8270C, SOP-329/231	4-ounce glass jar	15 grams	Cool to 4° C	14 days until extraction/40 days to analysis
Aqueous field Quality Control and IDW	Metals	SW-846 3005A/6010B SOP-100/105	500-milliliter plastic bottle	50 milliliters/30 milliliters mercury	HNO_3 to a pH<2; Cool to 4° C	180 days to analysis, 28 days to analysis for mercury
Soil	Metals	SW-846 3050B/6010B SOP-100/105	4-ounce glass jar	1 to 2 grams/ 0.3 grams mercury	Cool to 4° C	180 days to analysis, 28 days to analysis for mercury
Solid IDW	TCLP VOCs	SW-846 1311/8260B/ Empirical SOP-198/202	4-ounce glass jar	100 grams	Cool to 4° C	14 days to TCLP extraction/14 days for VOCs to analysis.
Solid IDW	TCLP Metals	SW-846 1311/3005A/6010B/ 7470A Empirical SOP-198/100/105/103/104	4-ounce glass jar	100 grams	Cool to 4° C	14 days to TCLP extraction/180 days to analysis, 28 days to analysis for mercury

Matrix	**Analytical Group**	**Analytical and Preparation Method/SOP Reference[1]**	**Containers** (number, size, and type)	**Sample volume[2]** (units)	**Preservation Requirements** (chemical, temperature, light protected)	**Maximum Holding Time[3]** (preparation/ analysis)
Aqueous IDW	Reactivity/Ignitibility/ Corrosivity/pH	SW-846 9012A/Chapter 7/1010/9040 Empirical SOP-149/156/164/175/187	Cyanide - plastic, Sulfide - glass, pH - plastic	500 milliliters Cyanide and Sulfide, 50 ml pH	Cyanide-NaOH to pH>12, Sulfide-Zinc acetate and NaOH to>pH 9 and all cool to 4° C	Cyanide -14 days, sulfide - 7 days, Ignitability and pH ASAP
Solid IDW	Reactivity/Ignitibility/ Corrosivity/pH	SW-846 9012A/Chapter 7/1010/9045C Empirical SOP-149/156/164/175/187	4 to 8-ounce glass jar	4 ounces	Cool to 4° C	14 days Cyanide/7 days Sulfide /ASAP for Ignitability. and pH
Soil	pH	SW-846 9045C Empirical SOP-187	4-ounce glass jar	4 ounces	Cool to 4° C	ASAP
Soil	Total Organic Carbon	Lloyd Kahn Empirical SOP-221	4-ounce glass jar	5 grams	Cool to 4° C	28 days to analysis
Aqueous IDW	Total Petroleum Hydrocarbons	TX1005 TestAmerica SOP SA04-157	Two-40-milliliter VOA vials	5 milliliters	Hydrochloric acid to pH <2, Cool to 4° C, -12° C after extraction	14 days to extraction/14 days to analysis
Solid IDW	Total Petroleum Hydrocarbons	TX1005 TestAmerica SOP SA04-157	Two-40-milliliter VOA vials	10 grams	Samples and extracts should be cooled to -12° C	14 days to extraction/14 days to analysis
Soil	Cation Exchange Capacity	SW-846 9081	4-ounce glass jar	1 to 10 grams	NA	6 months to analysis

1 Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).
2 Provide the minimum sample volume or mass requirement if it differs from the container volume.
3 Maximum holding time is calculated from the time the sample is collected to the time the sample is prepared/extracted.

SAP Worksheet No. 20 -- Field Quality Control Sample Summary Table

(UFP-QAPP Manual Section 3.1.1)
SKEET RANGE

Field-Portable X-Ray Fluorescence (FPXRF) Analyses

Matrix	Analytical Group	Concentration Level	No. of Sampling Locations	No. of Field Duplicates	No. of MS/MSDs	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Solid	Lead	Low to Moderate	80	NA	NA	NA	NA	NA	NA

Fixed-Base Laboratory Analyses

Matrix	Analytical Group	Concentration Level	No. of Sampling Locations (1, 2),	No. of Field Duplicates (3)	No. of MS/MSDs (4)	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab(5)
Solid	Select Metals	Low to Moderate	18	2	1	NA	1	NA	21
Solid	PAHs	Low to Moderate	18	2	1	NA	1	NA	21
Solid	TOC	Low to Moderate	3	NA	NA	NA	NA	NA	3
Solid	CEC	Low to Moderate	3	NA	NA	NA	NA	NA	3
Solid	pH	Low to Moderate	3	NA	NA	NA	NA	NA	3
Solid IDW	TCLP Volatiles	Low to Moderate	1	NA	NA	NA	NA	NA	1
Solid IDW	TCLP Metals	Low to Moderate	1	NA	NA	NA	NA	NA	1
Solid IDW	RCI	Low to Moderate	1	NA	NA	NA	NA	NA	1

Matrix	Analytical Group	Concentration Level	No. of Sampling Locations (1, 2),	No. of Field Duplicates (3)	No. of MS/MSDs (4)	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab(5)
Solid IDW	TPH	Low to Moderate	1	NA	NA	NA	NA	NA	1
Water IDW	TCLP VOC	Low to Moderate	1	NA	NA	NA	NA	NA	1
Water IDW	TCLP Metals	Low to Moderate	1	NA	NA	NA	NA	NA	1
Water IDW	RCI	Low to Moderate	1	NA	NA	NA	NA	NA	1
Water IDW	TPH	Low to Moderate	1	NA	NA	NA	NA	NA	1

1 Minimum number of samples. Additional samples may be collected at different depths at the same location, with each discrete sampling depth counting as a separate sampling location or station.
2 If samples will be collected at different depths at the same location, count each discrete sampling depth as a separate sampling location or station.
3 Duplicates will be collected at a frequency of 1 per 10 samples.
4 Although MS/MSDs are not field QC samples, they are included here because location determination is often established in the field. Matrix Spike/Matrix Spike Duplicate (MS/MSD) will be collected at a frequency of 1 per 20 samples.
5 Total number of samples does not include MS/MSD samples.

SAP Worksheet No. 21 -- Project Sampling SOP References Table

(UFP-QAPP Manual Section 3.1.2)

Reference Number	Title, Revision Date and/or Number	Originating Organization of Sampling SOP	Equipment Type	Modified for Project Work? (Y/N)	Comments
SOP-01	Sample Labeling	TtNUS	NA	N	SOP Contained in Appendix B
SOP-02	Sample Identification Nomenclature	TtNUS	NA	N	SOP Contained in Appendix B
SOP-03	Sample Custody and Documentation of Field Activities	TtNUS	NA	N	SOP Contained in Appendix B
SOP-04	Decontamination of Field Sampling Equipment	TtNUS	NA	N	SOP Contained in Appendix B
SOP-05	Soil Coring and Sampling Using Hand Auger Techniques	TtNUS	NA	N	SOP Contained in Appendix B
SOP-09	Management of Investigation-Derived Waste	TtNUS	NA	N	SOP Contained in Appendix B
SOP-10	Borehole and Soil Sample Logging	TtNUS	NA	N	SOP Contained in Appendix B
SOP-11	Sample Preservation, Packaging, and Shipping	TtNUS	NA	N	SOP Contained in Appendix B
SOP-14	Use of Field Portable X-Ray Fluorescence Analysis of Soil and Sediment	TtNUS	Portable X-Ray Fluorescence analyzer and accessories	N	SOP Contained in Appendix B

SAP Worksheet No. 22 -- Field Equipment Calibration, Maintenance, Testing, and Inspection Table

(UFP-QAPP Manual Section 3.1.2.4)

Field Equipment	Activity[1]	Frequency	Acceptance Criteria	Corrective Action	Resp. Person	SOP Reference[2]	Comments
XRF	Verification/ standardization check	Prior to daily use and after every 20 samples throughout the day	No lead above QL limits for the instrument and method blanks	Restandardize. If still unacceptable, contact manufacturer for possible replacement	FOL	SOP-14	
GPS	Testing	Prior to daily use	Manufacturer's guidance	Operator correction or replacement	FOL	NA	

1 Activities may include calibration, verification, testing, maintenance.

2 Referenced SOPs can be found in Appendix B.

SAP Worksheet No. 23 -- Analytical SOP References Table

(UFP-QAPP Manual Section 3.2.1)

Lab SOP Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix and Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
Empirical SOP-100	Metals Digestion/Preparation Methods 3005A,3010A, 3020A, 3030, 3040A, 3050B, USEPA CLP ILM 04.1 Aqueous & Soil/Sediment, USEPA Method 200.7 (Standard Methods) 3030C. Rev. 19	Definitive	Soil/Metals	NA/Metals	Empirical	N
Empirical SOP-105	Metals Analysis by ICP Technique Methods 200.7, SW846 6010B, SM 19th Edition 2340B, USEPA ILM 04.1, Rev. 13	Definitive	Soil/Metals	ICP	Empirical	N
Empirical SOP-103	Mercury Analysis in Water by Manual Cold Vapor Technique Methods SW846 7470A & 245.1, CLP-M 4.1, Rev. 13	Definitive	Leachate and Aqueous IDW/Metals	Flow injection mercury analyzer	Empirical	N
Empirical SOP-104	Mercury Analysis in Soil/Sediment by Manual Cold Vapor Technique Methods SW846 7471A & 245.5, CLP-ILM 04.1, Rev. 15	Definitive	Soil/Metals	Flow injection mercury analyzer	Empirical	N
Empirical SOP-149	Flashpoint Ignitibility Method SW-846 1010, Rev. 1	Definitive	Aqueous and Solid IDW/Ignitability	Flashpoint Tester	Empirical	N
Empirical SOP-156	Reactive Sulfide Method SW-846, Chapter 7, Section 7.3.4, Rev. 4	Definitive	Aqueous and Solid IDW/Reactivity	NA	Empirical	N
Empirical SOP-164	Distillation of Aqueous/Solid Samples for Total and Non-Amenable Cyanide Analysis Methods 335.1/335.4, SW-846 9012A/USEPA CLP ILM 04.1, Rev. 12	Definitive	Aqueous and Solid IDW/Reactivity	Lachat	Empirical	N
Empirical SOP-175	Post-Distillation Analysis for Cyanide By the LACHAT Methods 335.4;SW846 9012A;USEPA-CLP 4.1;Addendum for USEPA CLP ILM 05.2 Aqueous & Soil/Sediment , Rev. 9	Definitive	Aqueous and Solid IDW/Reactivity	Lachat	Empirical	N
Empirical SOP-187	Electrometric Determination of pH, Methods 150.1, Standard Methods 4500H+B and 9040B for Waters, Liquids and Liquid Wastes, 9045C for Soils and Solid Wastes, Rev. 6	Definitive	Aqueous and Solid IDW/Corrosivity/pH	pH Meter	Empirical	N

Lab SOP Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Matrix and Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
Empirical SOP-198	Toxicity Characteristic Leaching Procedure (Method 1311), Rev. 5	Definitive	Solid IDW/Metals and VOCs	NA	Empirical	N
Empirical SOP-202	GC/MS Volatiles by Method 624 and SW-846 Method 8260B, Rev. 20	Definitive	Aqueous IDW and Leachate/VOCs	Agilent/HP GC/MS	Empirical	N
Empirical SOP-221	Total Organic Carbon SM5310C, USEPA Method 415.1 and SW-846 Method 9060 and Lloyd Kahn Method, Rev. 6	Definitive	Soil/TOC	TOC Analyzer	Empirical	N
Empirical SOP-231	GC/MS Low Level PAH By USEPA Method 625 and SW-846 Method 8270C, Rev. 1	Definitive	Soil/PAHs	Agilent/HP GC/MS	Empirical	N
Empirical SOP-300	GC/MS-Semivolatile BNA-Aqueous Matrix Extraction Using SW-846 Method 3510C for 8270C/625 Analysis, Rev. 16	Definitive	Aqueous/Extraction	NA/Extraction	Empirical	N
Empirical SOP-329	Soxhlet Extraction- BNA and Pest/PCB Using SW-846 Method 3541, Rev. 15	Definitive	Soil/Extraction	NA/Extraction	Empirical	N
Empirical SOP-404	Laboratory Sample Receiving Log-in and Storage Standard Operating Procedures, Rev. 11	Definitive	Log-in	NA/Log-in	Empirical	N
Empirical SOP-405	Analytical Laboratory Waste Disposal, Rev. 4	Definitive	Log-in	NA/Log-in	Empirical	N
Empirical SOP-410	Standard Operating Procedures for Laboratory Sample Storage, Secure Areas, and Sample Custody, Rev. 5	Definitive	Log-in	NA/Log-in	Empirical	N
TestAmerica SA04-157	TNRCC Method 1005: TNRCC Method for Total Petroleum Hydrocarbons Characterization of C6 to C35 Petroleum Hydrocarbons, Rev. 4	Definitive	Aqueous and Solid IDW/TPH	GC/FID	Test America	N
SW-846 9081	Cation Exchange Capacity of Soils SW-846 Method 9081	Definitive	Soil/CEC	ICP	Empirical	N

ICP = Inductively Coupled Plasma
GC = Gas Chromatograph
FID = Flame Ionization Detector
GC/MS = Gas Chromatography/Mass Spectrometer

SAP Worksheet #24 -- Analytical Instrument Calibration Table
(UFP-QAPP Manual Section 3.2.2)

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Gas Chromatograph/ Mass Spectrometer (Volatiles)	Initial Calibration - A minimum five point calibration is required.	Calibrate the instrument when it is received and after a major change or if the daily calibration fails.	The percent relative standard deviation (RSD) for each Calibration Check Compound (CCCs) must be ≤ 30%. The minimum mean response factor (RF) for each System Performance Check Compound (SPCCs) must meet that stated in 8260B. If the RSD for an analyte is > 15%, use a linear curve (≥ 0.995 correlation) or quadratic curve (≥0.99 correlation, minimum six points) for quantitation	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/Supervisor	Empirical SOP-202
	Initial calibration Verification (ICV)	Once after each initial calibration.	±20% recovery of individual compounds.	Identify source of problem, correct, repeat calibration, rerun samples	Analyst/Supervisor	
	Continuing Calibration (CCV)	Analyze a standard at the beginning of each 12-hour shift after a Bromofluorobenzene (BFB) tune.	The minimum RF for SPCCs must meet that stated in method. The CCCs must be < 20 percent difference.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/Supervisor	

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Gas Chromatograph/ Mass Spectrometer (PAHs)	Initial Calibration - A minimum 5 point calibration is required.	Calibrate the instrument when it is received and after a major change or if the daily calibration fails. A minimum five point calibration is required.	The RSD for each CCCs must be ≤ 30%. The minimum mean RF for each SPCCs must meet that stated in 8270C. If the RSD for an analyte is > 15%, use a linear curve (≥ 0.995 correlation) or quadratic curve (≥0.99 correlation, minimum six points) for quantitation.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/Supervisor	Empirical SOP-231
	Initial Calibration Verification (ICV)	Once after each initial calibration.	±20% recovery individual compounds.	Identify source of problem, correct, repeat calibration, rerun samples	Analyst/Supervisor	
	Continuing Calibration(CCV)	Analyze a standard at the beginning of each 12-hour shift after a decafluorotriphenyl phosphine (DFTPP) tune.	The minimum RF for SPCCs must meet those stated in method. The CCCs must be < 20 percent difference.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/Supervisor	

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Inductively Coupled Plasma (metals and CEC)	Initial Calibration	The instrument is calibrated at the beginning of each day or if the QC is out of criteria.	The instrument is calibrated by a one-point calibration per manufacturer's guidelines. Analytes ran at their calibration levels must fall within 90 to 110% of the true values.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/Supervisor	Empirical SOP-105
	Initial Calibration Blank (ICB)	Before beginning a sample sequence.	No analytes detected > 2x MDL.	Correct the problem, then re-prepare and reanalyze.	Analyst/Supervisor	
	Continuing Calibration(CCV)	Analyze a standard at the beginning and end of the sequence and after every 10 samples.	The acceptance criterion for the continuing calibration standard is 90 to 110% recovery of true value.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/Supervisor	
	Continuing Calibration Blank (CCB)	After every ten samples and at the end of the sequence.	No analytes detected > 2x MDL.	Correct the problem, then re-prepare and reanalyze calibration blank and previous ten samples.		

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Flow Injection Mercury System	Initial Calibration	The instrument is calibrated at the beginning of each day or if the QC is out of criteria.	The calibration correlation coefficient is $\geq$0.995.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/Supervisor	Empirical SOP-103/104
Flow Injection Mercury System	Continuing Calibration(CCV)	The CCV is analyzed at the beginning and end of the sequence and after every 10 samples.	The acceptance criteria are 80 to 120% recovery of the true value.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/Supervisor	Empirical SOP-103/104

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
OI 1010 Soil TOC Analyzer	Five point calibration including blank	Instrument receipt, instrument change, when continuing calibration verification does not meet criteria.	Correlation coefficient $\geq$ 0.995	Recalibrate and/or perform necessary equipment maintenance. Check calibration standards.	Analyst/ Supervisor	Empirical SOP-221
	Continuing calibration	After every 5 samples	80-120%	Recalibrate and/or perform necessary equipment maintenance. Check calibration standards.	Analyst/ Supervisor	Empirical SOP-221
FPXRF (Field Analysis)	Initial calibration - Per manufacturer's recommendations	Per manufacturer's recommendations	Per manufacturer's recommendations	Repeat calibration and/or contact instrument manufacturer	Analyst/supervisor	Tt SOP-14
	Continuing calibration - Per manufacturer's recommendations	One set per 20 samples analyzed after the instrument and method blanks	70% to 130% recovery	Per manufacturer's recommendations	Analyst/supervisor	Tt SOP-14
Lachat (reactivity)	Initial Calibration	The instrument is calibrated after an instrument change or if QC is outside criteria.	The correlation coefficient is >0.995.	Recalibrate and/or perform necessary equipment maintenance. Check calibration standards.	Analyst/Supervisor	Empirical SOP-175
	Continuing Calibration	The continuing calibration is analyzed at the beginning and end of the sequence and after every 10 samples.	The acceptance limits are 90 to 110% of the true value.	Recalibrate and/or perform necessary equipment maintenance. Reanalyze samples not bracketed by passing continuing calibration.	Analyst/Supervisor	Empirical SOP-175

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Flashpoint Tester (ignitability)	Flashpoint of p-xylene	Calibrate at the beginning and end of each set of 20 samples or less.	Flash at 27° C + 2.2° C.	Check standard	Analyst/Supervisor	Empirical SOP-149
pH Meter (pH/corrosivity)	Calibration	Before use with two buffers in area to be measured, check with third buffer	0.05 pH units	Recalibrate and/or perform necessary equipment maintenance.	Analyst/Supervisor	Empirical SOP-187
Gas Chromatograph/ Flame Ionization Detector (TPH)	Initial Calibration	Calibrate the instrument when it is received and after a major change or if the daily calibration fails. A minimum five point calibration is required.	Use average RF if %RSD < 25%. If greater, use linear regression. Correlation must be at least 0.995 and coefficient of determination (r^2) > 0.99	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/Supervisor	TestAmerica SA04-157
Gas Chromatograph/ Flame Ionization Detector (TPH)	Continuing Calibration	Analyze a midpoint standard at the beginning and end of each batch of 20 samples.	Percent difference < 25%	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/Supervisor	TestAmerica SA04-157

SAP Worksheet No. 25 -- Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

(UFP-QAPP Manual Section 3.2.3)

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Gas Chromatograph/ Mass Spectrometer	Clean the source and replace the filaments. Replace the seal, liner, and septum. Change the column.	Volatiles	Check the gas supply. Check the seal, liner, and septum.	Source cleaning is performed when the instrument response deteriorates. Other instrument maintenance is done as needed to keep the instrument performing at peak performance.	The minimum RF for SPCCs must meet those stated in method. The CCCs must be ≤ 20% difference.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/ Supervisor	Empirical SOP-202
Gas Chromatograph/ Mass Spectrometer	Clean the source and replace the filaments. Replace the seal, liner, and septum. Change the column.	PAHs	Check the gas supply. Check the seal, liner, and septum.	Source cleaning is performed when the instrument response deteriorates. Other instrument maintenance is done as needed to keep the instrument performing at peak performance.	The PAH compounds must be ≤ 20% difference.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/ Supervisor	Empirical SOP-231

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person[2]	SOP Reference[1]
Gas Chromatograph/ Flame Ionization Detector	Check pressure and gas supply daily. Bake out column, change septa, liner, seal as needed, cut column as needed.	TPH	Liner, seal, septum, and column.	Prior to initial calibration or as necessary.	Percent difference ≤ 25%.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/ Supervisor	TestAmerica SA04-157
Inductively Coupled Plasma Spectrometer	Clean the torch assembly and spray chamber when they become discolored or when degradation in data quality is observed. Clean the nebulizer and check the argon supply. Replace the peristaltic pump tubing as needed.	CEC and Metals	Inspect the torch, nebulizer chamber, pump, and tubing.	Maintenance is performed prior to initial calibration or as necessary.	The acceptance criteria for the continuing calibration standard are 90 to 110% of true value.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/ Supervisor	Empirical SOP-105 and SW-846 9081
Flow Injection Mercury System	Change the tubing and filter, clean windows, and check gas flow. Check the reagents and standards.	Mercury	Inspect the tubing, filter, and optical cell.	Maintenance is performed prior to initial calibration or as necessary.	The acceptance criteria are 80 to 120% of the true value.	Recalibrate and/or perform the necessary equipment maintenance. Check the calibration standards. Reanalyze the affected data.	Analyst/ Supervisor	Empirical SOP-103/104

Instrument / Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person[2]	SOP Reference[1]
Lachat	Degas solutions, change tubing and lamp, and clean connectors.	Cyanide/ Reactivity	Tubing and rollers.	Prior to initial calibration or as necessary.	The acceptance limits are 90 to 110% of the true value.	Recalibrate and/or perform necessary equipment maintenance. Reanalyze samples not bracketed by passing continuing calibration.	Analyst/ Supervisor	Empirical SOP-175
TOC Analyzer	Check gas pressure, check permeation tube and scrubbers, clean and condition sample cups.	TOC	Check gas pressure, check permeation tube and scrubbers.	Prior to initial calibration or as necessary.	The midpoint standard must be within 20% difference.	Recalibrate and/or perform necessary equipment maintenance. Reanalyze samples not bracketed by passing continuing calibration.	Analyst/ Supervisor	Empirical SOP-221
Flashpoint Tester	Change propane tank and calibrate thermometer.	Flashpoint/ Ignitability	Tank and thermometer.	Before use.	Flash at 27° C ± 2.2° C	Check standard.	Analyst/ Supervisor	Empirical SOP-149
pH Meter	Clean, drain, and refill reference electrode as needed.	pH/Corrosivity	Reference electrode for white crystals. Inspect electrode for damage.	Before use.	0.05 pH units	Recalibrate and/or perform necessary equipment maintenance.	Analyst/ Supervisor	Empirical SOP-187

SAP Worksheet No. 26 -- Sample Handling System

(UFP-QAPP Manual Appendix A)

Sample Handling System

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): TBD
Sample Packaging (Personnel/Organization): TBD
Coordination of Shipment (Personnel/Organization): TBD
Type of Shipment/Carrier: Federal Express
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Sample Custodians/Empirical Laboratories, LLC
Sample Custody and Storage (Personnel/Organization): Sample Custodians/Empirical Laboratories, LLC
Sample Preparation (Personnel/Organization): Extraction Lab, Metals Preparation Lab/Empirical Laboratories, LLC
Sample Determinative Analysis (Personnel/Organization): GC Lab, Gas Chromatography/Mass Spectrometry Lab, Metals Lab/Empirical Laboratories, LLC
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): 60 days from receipt
Sample Extract/Digestate Storage (No. of days from extraction/digestion): 3 months from sample digestion/extraction
Biological Sample Storage (No. of days from sample collection): NA
SAMPLE DISPOSAL
Personnel/Organization: Sample Custodians/Empirical Laboratories, LLC
Number of Days from Analysis: 30 days from submittal of final report or 60 days from receipt, whichever is longer

SAP Worksheet No. #27 – Sample Custody Requirements Table
(UFP-QAPP Manual Section 3.3.3)

1. SAMPLE CUSTODY REQUIREMENTS

Laboratory sample custody procedures (receipt of samples, archiving, disposal) will be according to Empirical SOPs 404, 405, and 410. As received coolers will be checked for proper temperature. A sample cooler receipt form will be completed to note conditions and any discrepancies. The chain-of-custody form will be checked against the sample containers for correctness. Samples will be logged into the Laboratory Information Management System (LIMS) and given a unique log number that can be tracked through processing. TtNUS will be notified of any problems.

Laboratory Identification Procedures: Empirical SOPs 404, 405, 410

Sample Identification Procedures: TtNUS SOP-02

Chain-of-Custody Procedures: TtNUS SOP-03

2. SAMPLE NOMENCLATURE

Sample Identification

Samples collected will be identified as described in TtNUS SOP-02.

The alphanumeric coding to be used is explained in the following diagram and subsequent definitions.

AA	AA	NN	NNNN
Site Acronym	Matrix	Sample Location Number	Sequential depth interval

Character Type:
A = Alpha
N = Numeric

Site Name (NN):
SR = Skeet Range

Matrix Code (AA):
SS = Surface Soil Sample
SB = Subsurface Soil Sample
SD = Sediment Sample

Location Number (NN):
Sequential number beginning with “01” for each matrix.

Depth Interval:
This code section will be used for soil samples only.

The depth code is used to note the depth bgs at which a soil sample is collected. The first two numbers of the four-number code specify the top interval, and the third and fourth specify the bottom interval in feet (soil) bgs of the sample. The depths will be noted in whole numbers only; further detail, if needed, will be recorded on the sample log sheet or boring log or in the logbook.

Field QA/QC samples will be designated using a different coding system than the one used for regular field samples. The QC code will consist of a three- to four-segment alpha-numeric code that identifies the

sample QC type, the date the sample was collected, and the number of this type of QC sample collected on that date.

AA	NNNNNN	NN
QC Type	Date	Sequence Number (per day)

Character Type:

A = Alpha
N = Numeric

QC Types:

FD = Field Duplicate
RB = Rinsate Blank
FB = Source Blank

The sampling time recorded on the chain-of-custody form, labels, and tags for field duplicate samples will be 0000 so that the samples are "blind" to the laboratory. Notes detailing the sample number, time, date, and type will be recorded on the sample log sheets and will document the location of the duplicate sample (sample log sheets are not provided to the laboratory).

3. SAMPLE COLLECTION DOCUMENTATION, HANDLING, TRACKING, AND CUSTODY PROCEDURES

Sample Collection Documentation

Field observations will be documented in a field logbook and/or on field log sheets including sample collection logs, boring logs, and monitoring well construction logs. Bound water-resistant field logbooks will be utilized for this project. All pages of each logbook will be recorded sequentially, and observations will be recorded with indelible ink.

Field sample log sheets will be used to document sample collection details, and other observations and activities will be recorded in the field logbook. Daily instrument calibration will be recorded on instrument calibration logs. Example field forms are included in Appendix C.

For sampling and field activities, the following types of information will be recorded in the field logbook as appropriate:

- Site name and location
- Date and time of logbook entries
- Personnel and their affiliations
- Weather conditions
- Activities associated with sampling
- Subcontractor activity summary
- Site observations including site entry and exit times
- Site sketches made on site
- Visitor names, affiliations, and arrival and departure times
- Health and safety issues including personal protective equipment (PPE)

Sample Handling and Tracking System

Procedures that will be used by field and laboratory personnel to document project activities and sample collection procedures during this SI are outlined in the following subsections. All forms will be completed in as completely as possible.

Sample Handling

Sample handling is described in SAP Worksheet No. 26.

Sample Delivery

Samples will be delivered to the laboratory via a public courier (i.e., Federal Express). Samples will be sent to the laboratory within 48 hours of being collected. Under no circumstances should sample holding times be exceeded.

Sample Custody

To ensure the integrity of a sample from collection through analysis, it is necessary to have an accurate written record that traces the possession and handling of the sample. This documentation is referred to as the chain-of-custody form. Chain of custody begins at the time of sample collection.

A sample is under custody if:

- It is in your actual possession, or
- It is in your view after being in your physical possession, or
- It was in your possession and then you locked or sealed it to prevent tampering, or
- It is in a secure area.

Custody documentation is designed to provide documentation of preparation, handling, storage, and shipping of all samples collected. A multi-part chain-of-custody form is used, with each page of the form signed and dated by the recipient of a sample or portion of sample. The person releasing the sample and the person receiving the sample each will retain a copy of the chain-of-custody form each time a sample transfer occurs.

Preservation of the integrity of the samples collected during the SI will be the responsibility of identified persons from the time the samples are collected until the samples, or their derived data, are incorporated into the final report.

The FOL is responsible for the care and custody of the samples collected until they are delivered to the laboratory or are entrusted to a carrier. When transferring samples, the individuals relinquishing and receiving them will sign, date, and note the time on the chain-of-custody form. This form documents the sample custody transfer from the sampler to the laboratory, often through another person or agency (common carrier). Upon arrival at the laboratory, internal sample custody procedures will be followed as defined in the laboratory SOPs included in Appendix C.

SAP Worksheet No. 28 -- Laboratory QC Samples Table

(UFP-QAPP Manual Section 3.4)

Matrix	Aqueous IDW and TCLP Leachate
Analytical Group	Volatiles
Analytical Method / SOP Reference	SW-846 8260B/Empirical SOP-202

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per batch of 20 or less samples.	No target compounds should be ≥ 1/2 the quantitation limit (QL) except common laboratory contaminants which should be < QL.	Reclean, retest, re-extract, reanalyze, and/or qualify the data.	Analyst, Laboratory Supervisor, and Data Validator.	Bias/Contamination	No target compounds > than ½ the QLs.
Surrogate	Three per sample.	Laboratory derived limits.	Reprepare and reanalyze for confirmation of matrix interference when appropriate.	Analyst, Laboratory Supervisor, and Data Validator.	Accuracy/Bias	Laboratory-derived limits: Dibromofluoromethane 85-120% recovery 1,2-Dichloroethane-d4 85-130% recovery Toluene-d8 85-115% recovery Bromofluorobenzene 80-120% recovery
Laboratory Control Sample (LCS)	One per batch of 20 or less samples.	The minimum of DoD QSM limits and laboratory-derived limits.	(1) Evaluate and reanalyze if possible (2) If an MS/MSD was performed in the same 12 hour clock and acceptable ,narrate. (3) If the LCS recoveries are high but the sample results are <QL, narrate. Otherwise reprepare and reanalyze the batch.	Analyst, Laboratory Supervisor, and Data Validator.	Precision/Accuracy/Bias	The limits are provided in SOP-202.

Matrix	Aqueous IDW and TCLP Leachate
Analytical Group	Volatiles
Analytical Method / SOP Reference	SW-846 8260B/Empirical SOP-202

Internal Standard (IS)	Three per sample (Fluorobenzene, Chlorobenzene-d5, and 1,4-Dichlorobenzene-d4).	Retention times for internal standards must be ± 30 seconds and the responses within -50% to +100% of last continuing calibration (12 hours) for each internal standard.	Inspect mass spectrometer or gas chromatograph for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning.	Analyst, Laboratory Supervisor, and Data Validator.	Precision/Accuracy/Bias	Retention times for internal standards must be ± 30 seconds and the responses within -50% to +100% of last calibration verification (12 hours) for each internal standard.
Matrix spike / Matrix spike duplicate (MS/MSD)	One per SDG or every 20 samples.	The minimum of DoD QSM limits and laboratory-derived limits.	(1) Corrective action will not be taken for samples when recoveries are outside limits and surrogate and LCS criteria are met. (2) If both the LCS and MS/MSD are unacceptable, reprepare the samples and QC.	Analyst, Laboratory Supervisor, and Data Validator.	Precision/Accuracy/Bias	The limits are provided in SOP-202, same as specified for LCS.

Matrix	Water/Soil
Analytical Group	PAHs
Analytical Method/ SOP Reference	SW-846 8270C/Empirical SOP-231

QC Sample	Frequency / Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per batch of 20 or less	No target compounds should be ≥1/2 the QL except common laboratory contaminants, which should be < QL.	Reclean, retest, re-extract, reanalyze, and/or qualify the data.	Analyst, Laboratory Supervisor, and Data Validator.	Bias/Contamination	No target compounds > than ½ the QLs.
Surrogate	Three per sample	Laboratory-derived limits.	Reprepare and reanalyze for confirmation of matrix interference when appropriate.	Analyst, Laboratory Supervisor, and Data Validator.	Accuracy/Bias	Laboratory-derived limits: Aqueous: Nitrobenzene-d5 40-110% recovery 2-Fluorobiphenyl 50-110% recovery Terphenyl-d14 50-135% recovery Soil: Nitrobenzene-d5 35-100% recovery 2-Fluorobiphenyl 45-105% recovery Terphenyl-d14 30-125% recovery
Laboratory Control Sample (LCS)	One per batch of 20 or less	Laboratory-derived limits.	(1) Evaluate and reanalyze if possible (2) If an MS/MSD was performed in the same 12-hour clock and acceptable, narrate. (3) If the LCS recoveries are high but the sample results are <QL, narrate. Otherwise reprepare and reanalyze the	Analyst, Laboratory Supervisor, and Data Validator.	Precision/Accuracy/Bias	The limits are provided in SOP-231.

Matrix	Water/Soil
Analytical Group	PAHs
Analytical Method/ SOP Reference	SW-846 8270C/Empirical SOP-231

			batch.			
Internal Standard (IS)	Six per sample (Acenaphthene-d10 Chrysene-d12 1,4-Dichlorobenzene-d4 Naphthalene-d8 Perylene-d12 Phenanthrene-d10)	Retention times for internal standards must be ± 30 seconds and the responses within -50% to +100% of last calibration verification (12 hours) for each internal standard.	Inspect MS or GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning	Analyst, Laboratory Supervisor, and Data Validator.	Precision/Accuracy/Bias	Retention times for internal standards must be ± 30 seconds and the responses within -50% to +100% of last calibration verification (12 hours) for each internal standard.
Matrix spike/Matrix spike duplicate (MS/MSD)	One per SDG or every 20 samples.	Laboratory-derived limits.	(1) Corrective action will not be taken when recoveries are outside limits and surrogate and LCS criteria are met. (2) If both the LCS and MS/MSD are unacceptable, reprepare the samples and QC.	Analyst, Laboratory Supervisor, and Data Validator.	Precision/Accuracy/Bias	The limits are provided in SOP-231.

Matrix	Aqueous IDW and TCLP Leachate
Analytical Group	Metals
Analytical Method/ SOP Reference	SW-846 3005A, 6010B/7470A/SOP-100/103/105

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per digestion batch of 20 or fewer samples.	Contaminants in the method blank must be less than ½ the QL.	Investigate the source of the contamination. Redigest and reanalyze all associated samples if the sample concentration is ≥ the QL and <10x the blank concentration.	Analyst, Laboratory Supervisor, and Data Validator.	Bias/Contamination	Contaminants in the method blank must be less than 1/2 the QL.
Laboratory Control Sample (LCS)	One per digestion batch of 20 or fewer samples.	Recovery must be within ± 20% of the true value, unless vendor-supplied or statistical limits have been established.	(1) Investigate source of problem. (2) Redigest and reanalyze all associated samples.	Analyst, Laboratory Supervisor and Data Validator.	Accuracy/Bias/Contamination	Recovery must be within ± 20% of the true value, unless vendor-supplied or statistical limits have been established.
Duplicate Sample	One per digestion batch of 20 or fewer samples.	The relative percent difference should be within ≤20% for duplicate spikes.	Flag results.	Analyst, Laboratory Supervisor, and Data Validator	Precision	The relative percent difference should be within ≤20% for duplicate spikes.
Matrix Spike	One per digestion batch of 20 or fewer samples.	Recovery should be ± 25% of the true value, if sample < 4x spike added.	Flag results.	Analyst, Laboratory Supervisor, and Data Validator	Accuracy/Bias	Recovery should be ± 25% of the true value, if sample < 4x spike added.
ICP Serial Dilution	One per digestion batch.	If original sample result is at least 50x the instrument detection limit, 5-fold dilution must agree within ± 10% of the original result.	Flag result or dilute and reanalyze sample to eliminate interference.	Analyst, Laboratory Supervisor and Data Validator	Accuracy/Bias	If original sample result is at least 50x the instrument detection limit, five fold dilution must agree within ± 10% of the original result.

Matrix	Soil
Analytical Group	Metals
Analytical Method/ SOP Reference	SW-846 3050B, 6010B/7471A/SOP-100/104/105

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per digestion batch of 20 or fewer samples.	Contaminants in the method blank must be less than ½ the QL.	Investigate the source of the contamination. Redigest and reanalyze all associated samples if the sample concentration is ≥ the reporting limit and <10x the blank concentration.	Analyst, Laboratory Supervisor, and Data Validator.	Bias/Contamination	Contaminants in the method blank must be less than 1/2 the QL.
Laboratory Control Sample (LCS)	One per digestion batch of 20 or fewer samples.	Recovery must be within ± 20% of the true value, unless vendor-supplied or statistical limits have been established.	Investigate source of problem. Redigest and reanalyze all associated samples.	Analyst, Laboratory Supervisor, and Data Validator.	Accuracy/Bias/Contamination	Recovery must be within ± 20% of the true value, unless vendor-supplied or statistical limits have been established.
Duplicate Sample	One per digestion batch of 20 or fewer samples.	The relative percent difference should be within ≤20% for duplicate spikes.	Flag results.	Analyst, Laboratory Supervisor, and Data Validator.	Precision	The relative percent difference should be within ≤20% for duplicate spikes.
Matrix Spike	One per digestion batch of 20 or fewer samples.	Recovery should be ± 25% of the true value, if sample < 4x spike added.	Flag results.	Analyst, Laboratory Supervisor, and Data Validator.	Accuracy/Bias	Recovery should be ± 25% of the true value, if sample < 4x spike added.
ICP Serial Dilution	One per digestion batch.	If original sample result is at least 50x the instrument detection limit, five-fold dilution must agree within ± 10% of the original result.	Flag result or dilute and reanalyze sample to eliminate interference.	Analyst, Laboratory Supervisor, and Data Validator.	Accuracy/Bias	If original sample result is at least 50x the instrument detection limit, five fold dilution must agree within ± 10% of the original result.

Matrix	Solid and Aqueous IDW
Analytical Group	Reactivity/Cyanide
Analytical Method/ SOP Reference	SW-846 9012A/ SOP-175

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Distilled Preparation Blank	Every batch of 20 samples or less.	Less than ½ the QL.	If there is an instrument problem, reanalyze preparation blank. If there is a distillation problem, samples 5x the preparation blank can be reported. If < than the QL, re-distill and reanalyze.	Analyst, Laboratory Supervisor, and Data Validator.	Bias/Contamination	Be less than 1/2 the QL.
LCS	Every batch of 20 samples or less.	80-120% recovery	Reanalyze when instrument is in control. If recovery is low, redigest and reanalyze samples. If recovery is high and there are positive detections, redigest and reanalyze.	Analyst, Laboratory Supervisor, and Data Validator.	Accuracy/Bias	80-120% recovery
Distilled Calibration Verification	Every batch of 20 samples or less.	90-110% recovery	Check with supervisor before proceeding.	Analyst, Laboratory Supervisor and Data Validator.	Accuracy / Bias	90-110% recovery
MS/MSD	Every batch of 20 samples or less.	80-120% recovery	Check with supervisor before proceeding.	Analyst, Laboratory Supervisor, and Data Validator.	Precision/Accuracy/Bias	80-120% recovery
Calibration Blanks	During sequence every 10 samples.	Less than the MDLs.	Check with supervisor before proceeding.	Analyst, Laboratory Supervisor, and Data Validator.	Bias/Contamination	Less than the MDLs.

Matrix	Solid and Aqueous IDW
Analytical Group	Reactivity/Sulfide
Analytical Method/ SOP Reference	SW-846 Chapter 7/ SOP-156

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	Every batch of 20 samples or less.	Less than ½ the QL.	Reanalyze, and/or qualify data.	Analyst, Laboratory Supervisor, and Data Validator.	Bias/Contamination	Less than 1/2 the QL.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Every batch of 20 samples or less.	80-120% recovery	Check with supervisor before proceeding.	Analyst, Laboratory Supervisor, and Data Validator.	Precision/Accuracy/Bias	80-120% recovery

Matrix	Solid and Aqueous IDW
Analytical Group	Ignitability/Flashpoint
Analytical Method/ SOP Reference	SW-846 1010/SOP-149

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
p-xylene flashpoint	At the beginning and end of each set of 20 samples.	27°C ± 2.2°C	Reanalyze, and/or qualify data.	Analyst, Laboratory Supervisor, and Data Validator.	Accuracy/Bias	27°C ± 2.2°C

Matrix	Soil
Analytical Group	Total Organic Carbon
Analytical Method/ SOP Reference	Lloyd Kahn/SOP-221

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per preparation batch of 20 or fewer samples.	No TOC detected above 1/2 QL.	Investigate source of contamination and reanalyze all affected samples.	Analyst, Supervisor, and QA Manager.	Accuracy/Bias-Contamination	No TOC detected above 1/2 QL.
Laboratory Duplicate	One per preparation batch of 10 or fewer samples.	Relative percent difference ≤ 50%	Narrate any results that are outside control limits.	Analyst, Supervisor, and QA Manager.	Precision	Relative percent difference ≤ 50%
Matrix Spike	One per preparation batch of 10 or fewer samples.	50-150% recovery	No corrective action will be taken for samples where recoveries are outside acceptance limits and LCS criteria are met. Narrate noncompliances.	Analyst, Supervisor, and QA Manager.	Accuracy/Bias	50-150 % recovery
Laboratory Control Sample	One per preparation batch of 20 or fewer samples.	80-120% recovery	Reanalyze associated samples. If the sample is within holding time, reanalyze affected sample batch. If the LCS recovery is high but the sample results are < the QL, narrate. Otherwise, reprepare the blank and affected sample batch.	Analyst, Supervisor, and QA Manager.	Accuracy/Bias	80-120% recovery

Matrix	Soil, Solid and Aqueous IDW
Analytical Group	pH/Corrosivity
Analytical Method/ SOP Reference	SW-846 9045C/ SOP-187

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory Duplicate	One per preparation batch of 10 or fewer samples.	± 0.09 units	Recalibrate and reanalyze samples.	Analyst, Supervisor, and QA Manager.	Precision	± 0.09 units
Laboratory Control Sample	Once per 20 samples.	± 0.25 units	Reanalyze associated samples.	Analyst, Supervisor, and QA Manager.	Accuracy/Bias	± 0.25 units

Matrix	Soil
Analytical Group	CEC
Analytical Method/ SOP Reference	SW-846 9081

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per preparation batch of 10 or fewer samples	Less than the QL.	Correct and reanalyze batch	Analyst, Supervisor, QA Manager	Accuracy/bias-Contamination	Less than the QL.
Laboratory Duplicate	One per preparation batch of 10 or fewer samples	< 20 relative percent difference	Report	Analyst, Supervisor, QA Manager	Precision	Percent recovery should be 75-125% or within laboratory limits< 20 relative percent difference

Matrix	Solid and Aqueous IDW
Analytical Group	TX TPH
Analytical Method/ SOP Reference	TX 1005/TestAmerica SA04-157

QC Sample	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	One per batch of 20 or less.	No target compounds should be $\geq$1/2 the QL.	Reclean, retest, reextract, reanalyze, and/or qualify the data.	Analyst, Laboratory Supervisor, and Data Validator	Bias/Contamination	No target compounds should be $\geq$ 1/2 the QL.
Surrogate	Two per sample	Percent recovery should be 75-125% or within laboratory limits	Reanalyze or re-extract and reanalyze, or flag the data.	Analyst, Laboratory Supervisor, and Data Validator	Accuracy/Bias	Percent recovery should be 75-125% or within laboratory limits
Laboratory Control Spike/Laboratory Spike Duplicate (LCS/LCSD)	One per batch of 20 or less.	Percent recovery should be 75-125% and relative percent difference $\leq$ 20% or within laboratory limits.	Correct the problem then reprepare and analyze LCS/LCSD and all samples in the affected analytical batch	Analyst, Laboratory Supervisor, and Data Validator	Precision/Accuracy/Bias	Percent recovery should be 75-125% and relative percent difference $\leq$ 20% or within laboratory limits.
Matrix Spike/ Matrix Spike Duplicate (MS/MSD)	Every batch of 20 samples or less.	Percent recovery should be 75-125% and relative percent difference $\leq$ 20% or within laboratory limits.	None	Analyst, Laboratory Supervisor, and Data Validator.	Precision/Accuracy/Bias	Percent recovery should be 75-125% and relative percent difference $\leq$ 20% or within laboratory limits.

SAP Worksheet No. 29 -- Project Documents and Records Table

(UFP-QAPP Manual Section 3.5.1)

Document	Where Maintained
Sample Collection Documents and Records Field logbook (and sampling notes) Field sample forms (e.g. boring logs, sample log sheets, drilling logs, etc.) Chain-of-custody records Sample shipment airbills Equipment calibration logs Photographs Field Task Modification Request Forms Sampling and Analysis Plan Field Sampling SOPs	TtNUS project file, results will be discussed in subject document.
Laboratory Documents and Records Sample receipt/log-in form Sample storage records Sample preparation logs Standard traceability logs Equipment calibration logs Sample analysis run logs Equipment maintenance, testing, and inspection logs Reported field sample results Reported results for standards, quality control checks, and quality control samples Data completeness checklists Sample storage and disposal records Telephone logs Extraction/clean-up records Raw data	TtNUS project file, long-term data package storage at third-party professional document storage firm, results will be discussed in subject document.
Data Assessment Documents and Records Field Sampling Audit Checklist (if an audit is conducted) Analytical Audit Checklist (if an audit is conducted) Data Validation Memoranda Site Inspection Report	TtNUS project file, results will be discussed in subject document.

SAP Worksheet No. 30 -- Analytical Services Table

(UFP-QAPP Manual Section 3.5.2.3)

Matrix	Analytical Group	Sample Locations/ID Number	Analytical Method	Data Package Turnaround Time	Laboratory/Organization (name and address, contact person and telephone number)	Backup Laboratory/ Organization (name and address, contact person and telephone number)
Aqueous Field Quality Control and Soil	Metals	See Worksheet No. 18	SW-846 6010B	28 calendar days	Janice Shilling Empirical 227 French Landing Nashville, TN 37228 615-345-1115	NA
Aqueous Field Quality Control and Soil	PAHs	See Worksheet No. 18	SW-846 8270C	28 calendar days	Janice Shilling Empirical 227 French Landing Nashville, TN 37228 615-345-1115	NA
Solid IDW	TCLP Volatiles and Metals	See Worksheet No. 18	SW-846 1311/8260B/6010B/7470A	28 calendar days	Janice Shilling Empirical 227 French Landing Nashville, TN 37228 615-345-1115	NA
Solid and Aqueous IDW	TPH	See Worksheet No. 18	TX 1005	28 calendar days	Elizabeth Eichelberger TestAmerica 4955 Yarrow St. Arvada, CO 80002 303-736-0138	NA
Solid and Aqueous IDW	Reactive Cyanide (reactivity)	See Worksheet No. 18	SW-846 9012A/ Method SW-846, Chapter 7, Section 7.3.4.	28 calendar days	Janice Shilling Empirical 227 French Landing Nashville, TN 37228 615-345-1115	NA

Matrix	Analytical Group	Sample Locations/ID Number	Analytical Method	Data Package Turnaround Time	Laboratory/Organization (name and address, contact person and telephone number)	Backup Laboratory/ Organization (name and address, contact person and telephone number)
Solid	Ignitability (flashpoint)	See Worksheet No. 18	SW-846 1010	28 calendar days	Janice Shilling Empirical 227 French Landing Nashville, TN 37228 615-345-1115	NA
Soil	CEC	See Worksheet No. 18	SW-846 9081	28 calendar days	Elizabeth Eichelberger TestAmerica 4955 Yarrow St. Arvada, CO 80002 303-736-0138	NA
Soil, Aqueous and Solid IDW	pH/ Corrosivity	See Worksheet No. 18	SW-846 9045C	28 calendar days	Janice Shilling Empirical 227 French Landing Nashville, TN 37228 615-345-1115	NA
Soil	TOC	See Worksheet No. 18	Lloyd Kahn	28 calendar days	Janice Shilling Empirical 227 French Landing Nashville, TN 37228 615-345-1115	NA

CEC - Cation exchange capacity
NA - Not applicable
TOC - Total organic carbon

SAP Worksheet No. 31 -- Planned Project Assessments Table

(UFP-QAPP Manual Section 4.1.1)

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (title and organizational affiliation)	Person(s) Responsible for Responding to Assessment Findings (title and organizational affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Action (CA) (title and organizational affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (title and organizational affiliation)
Field Supervision	Daily	Internal	TtNUS	TtNUS FOL	TtNUS FOL	TtNUS FOL and Field Crew	Tetra Tech FOL, TOM, QAM
Project Supervision	Monthly	Internal	TtNUS	TtNUS TOM	TtNUS FOL	TtNUS FOL	Tetra Tech TOM, FOL, Program Manager
Laboratory Systems Audit	Every 18 months	External	NFESC	NFESC	Laboratory QAM	Laboratory QAM	Laboratory QAM
Field Sampling Systems Audit	One per contract year	Internal	TtNUS	TBD	TOM	Auditor and TtNUS QAM	TtNUS QAM

SAP Worksheet No. 32 -- Assessment Findings and Corrective Action Responses

(UFP-QAPP Manual Section 4.1.2)

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (name, title, organization)	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (name, title, organization)	Timeframe for Response
Field Supervision	Site logbook	Ken Grim, TtNUS TOM; Larry Basilio, TtNUS FOL	Immediately	Entry in site logbook	Ken Grim, TtNUS TOM; Larry Basilio, TtNUS FOL	24 hours
Project Supervision	Written report	Debbie Humbert, Program Manager, TtNUS; Mark Perry, Deputy Program Manager TtNUS	Quarterly	Written memorandum	Ken Grim, TtNUS TOM	Within 1 week of notification
Field sampling System Audit	Audit checklist (as per IRCDQM) and written audit report	Ken Grim, TtNUS TOM; Larry Basilio, TtNUS FOL Debbie Humbert, Program Manager, TtNUS; Mark Perry, Deputy Program Manager TtNUS	Dependant on findings; if major, a stop work may be issued immediately; if minor, within 1 week of audit	Written memorandum	Kelly Carper, TtNUS QAM, TtNUS TBD, TtNUS Auditor, Debbie Humbert, CLEAN Program Manager, TtNUS	Within 4 weeks of notification
Laboratory Systems Audit	Written audit report	Randy Ward, Laboratory QAM, Empirical	Not specified by NFESC	Letter	NFESC	Specified by NFESC

FOL Field Operations Leader
IRCDQM Navy Installation Restoration Chemical Data Quality Manual
NFESC Naval Facilities Engineering Service Center
TOM Task Order Manager
QAM Quality Assurance Manager

SAP Worksheet No. 33 -- QA Management Reports Table

(UFP QAPP Manual Section 4.2)

Type of Report	Frequency (daily, weekly monthly, quarterly, annually, etc.)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (title and organizational affiliation)	Report Recipient(s) (title and organizational affiliation)
Data validation report	Per SDG	Within 3 weeks of receipt of complete laboratory data	DVM or designee TtNUS	TtNUS TOM and TtNUS project file
Major analysis problem identification (Internal memo)	When persistent analysis problems are detected	Immediately	QAM TtNUS	TtNUS TOM, TtNUS QAM, CLEAN Program Manager, TtNUS, and project file
Project monthly progress report	Monthly for duration of project	Monthly	TOM TtNUS	Navy RPM, project file
Field progress report	Daily, oral, during the course of sampling	Every day that field sampling occurs	FOL TtNUS	TtNUS TOM
Laboratory QA report	When significant plan deviations result from unanticipated circumstances	Immediately	Subcontracted laboratories	TtNUS QAM or Project Chemist, project file
Audit report	In conjunction with audits	After completion of audits (usually 3 weeks)	Auditor(s)	TtNUS TOM, TtNUS QAM, and audited entity

DVM – Data Validation Manager
FOL – Field Operations Leader
QAM – Quality Assurance Manager
TOM – Task Order Manager
SDG – Sample Delivery Group

SAP Worksheet No. 34 -- Verification (Step I) Process Table

(UFP-QAPP Manual Section 5.2.1)

Verification Input	Description	Internal / External	Responsible for Verification (name, organization)
Chain-of-custody forms	A TtNUS representative will review and sign the chain-of-custody form to verify that all samples listed are included in the shipment to the laboratory and that the sample information is accurate. The forms will be signed by the sampler, and a copy will be retained for the project file, TOM, and data validators. See SOP 10.	Internal	TtNUS, field personnel
QAPP sample tables	Verify that all proposed samples listed in the QAPP tables have been collected.	Internal	TtNUS, field personnel
Sample log sheets	Verify that information recorded in the log sheets is accurate and complete.	Internal	TtNUS, field personnel
Sample coordinates	Verify that sample locations are correct and in accordance with the QAPP proposed locations. Take into account the potential for locations to have been updated.	Internal	TtNUS, field personnel
Field QC samples	Check that field QC samples listed in Worksheet No. 20 were collected as required.	Internal	TtNUS, field personnel
Chain-of-custody forms	The laboratory sample custodian will review the sample shipment for completeness and integrity and will sign accepting the shipment. The data validators will check that the chain-of-custody form was signed/dated by the TtNUS field personnel relinquishing the samples and also by the laboratory sample custodian receiving the samples for analyses.	Internal/ External	1 - Laboratory sample custodian 2 - TtNUS, data validators
Analytical data package	All analytical data packages will be verified internally for completeness by the laboratory performing the work. The laboratory QAM will sign the case narrative for each data package.	Internal	Laboratory QAM

Verification Input	Description	Internal / External	Responsible for Verification (name, organization)
Analytical data packages	The data package will be verified for completeness by TtNUS data validators. Missing information will be requested from the laboratory, and validation will be suspended until missing data are received.	External	TtNUS, data validators
Analytical data packages and electronic data deliverables	The electronic data will be verified against the chain-of-custody and hard copy data package for accuracy and completeness. Laboratory analytical results will be verified and compared to the electronic analytical results for accuracy. Sample results will be evaluated for laboratory contamination and will be qualified for false positives using the laboratory method/preparation blank summaries. Positive results reported between the method detection limit and reporting limit will be qualified as estimated. Extraneous laboratory qualifiers will be removed from the validation qualifier.	External	TtNUS, data validators

FOL – Field Operations Leader
TOM – Task Order Manager
QAPP – Quality Assurance Project Plan

SAP Worksheet No. 35 -- Validation (Steps IIa and IIb) Process Table

(UFP-QAPP Manual Section 5.2.2) (Figure 37 UFP-QAPP Manual) (Table 9 UFP-QAPP Manual)

Step IIa / IIb	Validation Input	Description	Responsible for Validation (name, organization)
IIa	Field SOPs	Ensure that all sampling SOPs were followed and that any field deviations were documented.	TtNUS TOM, field personnel
IIa	Analytical SOPs	Ensure that the laboratory followed the analytical SOPs cited in the SAP and that any method deviations were approved by TtNUS and documented in the case narrative.	TtNUS project chemist or data validators
IIa	Analytical SOPs	Ensure that the field personal followed the SOP cited in this SAP for the field XRF analysis of lead.	TtNUS FOL and project chemist
IIa	Chain-of-custody forms	Ensure that the custody and integrity of the samples were maintained from collection to analysis and that custody records are complete and any deviations are recorded.	TtNUS project chemist or data validators
IIa	Holding times	Ensure that the samples were shipped and store at the required temperature and sample pH values for chemically preserved samples met the requirements listed in Worksheet No. 19. Verify that the analyses were performed within the holding times listed in Worksheet No. 19.	TtNUS project chemist or data validators
IIa	Data results	Check the summary form results against the raw data. Check calculations for accuracy.	TtNUS project chemist or data validators
IIa	Standards	Ensure that the standards used in the field and laboratory are traceable and meet the contract, method, and procedural requirements.	TtNUS project chemist or data validators
IIa/IIb	Laboratory data results for accuracy	Ensure that the laboratory QC samples listed in Worksheet No. 28 were analyzed and that the measurement performance criteria listed in Worksheet No. 12 were met for all field samples and QC analyses. Verify that specified field QC samples were collected and analyzed and that the analytical QC criteria set up for this project were met.	TtNUS project chemist or data validators
IIa/IIb	Field and laboratory duplicate analyses for precision	Ensure field sampling precision by checking the RPD for field duplicate samples. Verify laboratory precision by checking the RPD or percent difference values from laboratory duplicate analyses, matrix spike/matrix spike duplicates, and laboratory control sample/laboratory control sample duplicates. Ensure compliance with the methods and project MPC accuracy goals listed in Worksheets No. 12.	TtNUS project chemist or data validators
IIa/IIb	Sample results for representativeness	Ensure that the laboratory recorded the temperature at sample receipt and the pH of chemically preserved samples.	TtNUS project chemist or data validators

Step IIa / IIb	**Validation Input**	**Description**	**Responsible for Validation** (name, organization)
IIb	PQLs for sensitivity	Ensure that the project quantitation limits listed in Worksheet No. 15 were achieved.	TtNUS project chemist or data validators
IIa/IIb	Project action limits	Discuss the impact of matrix interferences or sample dilutions performed because of the high concentrations of one or more contaminants on other target compounds reported as non-detected. Document this usability issue and inform the TOM.	TtNUS project chemist or data validators
IIb	Analytical data deviations	Determine the impact of any deviation from sampling or analytical methods and SOPs requirements and matrix interferences effect on the analytical results.	TtNUS project chemist or data validators

SAP Worksheet No. 36 – Analytical Data Validation (Steps IIa and IIb) Summary Table

(UFP-QAPP Manual Section 5.2.2.1)

Step IIa / IIb	Matrix	Analytical Group	Validation Criteria	Data Validator
IIa and IIb	Aqueous and Soil	Metals	Criteria for SW-846 6010B/7470A-7471A listed in Worksheet Nos. 12, 15, 24, 25, and 28, TRRP 13, and DoD QSM (January 2006).	Data Validation Specialist (TtNUS)
IIa and IIb	Aqueous and Soil	PAHs	Criteria for SW-846 8270 listed in Worksheet Nos. 12, 15, 24, 25, and 28, TRRP 13, DoD QSM (January 2006).	Data Validation Specialist (TtNUS)

SAP Worksheet No. 37 -- Usability Assessment

(UFP-QAPP Manual Section 5.2.3)

Data Usability Assessment

The usability of the data directly affects whether project objectives can be achieved. The following characteristics will be evaluated at a minimum. The results of these evaluations will be included in the project report. The characteristics will be evaluated for multiple concentration levels if the evaluator determines that this is necessary. To the extent required by the type of data being reviewed, the assessors will consult with other technically competent individuals to render sound technical assessments of these data characteristics.

Completeness

- For each matrix that was scheduled to be sampled, the FOL acting on behalf of the project team will prepare a table listing planned samples/analyses to collected samples/analyses. If deviations from the scheduled sample collection or analyses are identified, the TtNUS TOM and risk assessor will determine whether the deviations compromise the ability to meet project objectives. If they do, the TtNUS TOM will consult with the Navy RPM and other project team members, as necessary (determined by the Navy RPM), to develop appropriate corrective actions.

Precision

- The Project Chemist acting on behalf of the project team will determine whether precision goals for field duplicates and laboratory duplicates were met. This will be accomplished by comparing duplicate results to precision goals identified in Worksheet Nos. 12 and 28. This will also include a comparison of field and laboratory precision with the expectation that field duplicate results will be no less precise than laboratory duplicate results. If the goals are not met, or if data have been flagged as estimated (J qualifier), limitations on the use of the data will be described in the project report.

Accuracy

- The Project Chemist acting on behalf of the project team will determine whether the accuracy/bias goals were met for project data. This will be accomplished by comparing percent recoveries of LCS, LCSD, MS, MSD, and surrogate compounds to accuracy goals identified in Worksheet No. 28. This assessment will include an evaluation of field and laboratory contamination; instrument calibration variability; and analyte recoveries for surrogates, matrix spike, and laboratory control samples. If the goals are not met, limitations on the use of the data

will be described in the project report. Bias of the qualified results and a description of the impact of identified non-compliances on a specific data package or on the overall project data will be described in the project report.

Representativeness

- A project scientist identified by the TtNUS TOM and acting on behalf of the project team will determine whether the data are adequately representative of intended populations, both spatially and temporally. This will be accomplished by verifying that samples were collected and processed for analysis in accordance with this SAP, by reviewing spatial and temporal data variations, and by comparing these characteristics to expectations. The usability report will describe the representativeness of the data for each matrix and analytical fraction. This will not require quantitative comparisons unless the professional judgment of the project scientist indicates that a quantitative analysis is required.

Comparability

- The Project Chemist acting on behalf of the project team will determine whether the data generated for this project are sufficiently comparable to historical site data generated by different methods and for samples collected using different procedures and under different site conditions. This will be accomplished by comparing overall precision and bias among data sets for each matrix and analytical fraction. This will not require quantitative comparisons unless the professional judgment of the Project Chemist indicates that such quantitative analysis is required.

Field XRF/Laboratory Lead Data Correlation

- The project statistician will evaluate the correlation of field XRF data to laboratory data. Factors considered in this evaluation will include the magnitude of the slope and intercept of the correlation equation, the distribution of data points across the plotted concentration range, and the value of the correlation coefficient. If the correlation coefficient is less than 0.65 or the plotted data do not appear to be well correlated according to standard statistical principles, limitations on the use of the data will be described in the project report.

Sensitivity

- The Project Chemist acting on behalf of the project team will determine whether project sensitivity goals listed in Worksheet No. 15 were achieved. The overall sensitivity and quantitation limits from multiple data sets for each matrix and analysis will be compared. If sensitivity goals are not achieved, limitations on the data will be described. The Project Chemist will enlist the help of the project risk assessor to evaluate deviations from planned sensitivity goals.

Project Assumptions and Data Outliers

- The TtNUS TOM and designated team members will evaluate whether project assumptions were valid. This will typically be a qualitative evaluation but may be supported by quantitative evaluations. The type of evaluation depends on the assumption being tested. Quantitative assumptions include assumptions related to data distributions (e.g., normal versus log-normal) and estimates of data variability. Potential outliers will be removed if a review of the associated documentation indicates that the results have an assignable cause the renders them inconsistent with the remainder of the data. During this evaluation, the team will consider whether outliers could be indications of unanticipated site conditions.

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

After the completion of data validation, the data and data quality will reviewed to determine whether sufficient data of acceptable quality are available for decision making. In addition to the evaluations described above, a series of inspections and statistical analyses will be performed to estimate these characteristics. The statistical evaluations will include simple summary statistics for target analytes, such as maximum concentrations, minimum concentrations, numbers of samples with non-detected results, numbers of samples with detected results, and proportions of samples with detected and non-detected results. The project team members identified by the TOM will assess whether the data collectively support the attainment of project objectives. They will consider whether any missing or rejected data have compromised the ability to make decisions or to make the decisions with the desired level of confidence. The data will be evaluated to determine whether missing or rejected data can be compensated for by other data. Although rejected data will generally not be used, there may be reason to use them in a weight-of-evidence argument, especially when they supplement data that have not been rejected. If rejected data are used, their use will be supported by technically defensible rationales.

For statistical comparisons and mathematical manipulations, non-detected values will be represented by a concentration equal to one-half the sample-specific reporting limit. Duplicate results (original and duplicate) will not be averaged for the purpose of representing the range of concentrations. However, the maximum concentration of the original and duplicate samples will be used to represent the concentration at a particular sampled location.

Identify the personnel responsible for performing the usability assessment:

The TtNUS TOM, Project Chemist, FOL, and Project Scientist will be responsible for conducting the listed data usability assessments. The data usability assessment will be reviewed with the Navy RPM, USEPA Project Manager, and TCEQ Project Manager. The review will take place either in a face-to-face meeting or teleconference, depending on the extent of identified deficiencies. If no significant deficiencies are identified, the data usability assessment will simply be documented in the project report and reviewed during the normal document review cycle.

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

The data will be presented in tabular format, including data qualifications such as estimation (J, UJ) or rejection (R). Written documentation will support the non-compliance estimated or rejected data results. The project report will identify and describe the data usability limitations and suggest resampling or other corrective actions, if necessary.

APPENDIX A

CONCEPTUAL SITE MODEL FOR THE SKEET RANGE

10-1 GENERAL INTRODUCTION AND PROBLEM DEFINITION FOR WORKSHEET #10

The primary objective of this MRP MRA/S SI is to determine if further response actions or remedial investigations are appropriate for any of the sites identified in the PA. The SI considers the background information provided in the PA and collects supplemental site-specific environmental data to further define the nature and extent of MC at the sites identified in the PA report. The SI is a secondary component of the CERCLA site evaluation process and is not intended to be a full-scale study of the nature and extent of contamination. The SI consists of a visual and detector-aided field inspection focused on identifying evidence of MC contamination using as a basis, available information from the PA, Archive Search Reports, and other existing information previously collected for the MRA/S. This information is used to delineate boundaries, collect broad site information, and assess the risk(s)/hazards(s) posed by any MC discovered at the site in order to support the final recommendations.

Table 10-1 summarizes the Skeet Range at the NALF Waldron that was evaluated in the installation's PA report (Malcolm Pirnie, 2005).

10-2 GENERAL NAVAL AIR LANDING FIELD WALDRON PROBLEM DEFINITION INFORMATION BASED ON THE PA REPORT

NALF Waldron is an OLF that supports Naval air training operations out of NASCC. NASCC, home to the Chief of Naval Air Training (CNATRA), maintains and operates facilities and provides services and material to support operations of aviation facilities of the Naval Air Training Command and other tenant activities. The general command assignment is pilot training, primarily focusing on primary and intermediate flight maneuvering and traffic pattern operations. Training Air Wing FOUR based at the main installation performs touch-and-go landing training between the main installation, NALF Waldron, and NALF Cabaniss, eight miles west of NASCC.

NALF Waldron (three miles south of NASCC) is one of six OLFs, constructed as auxiliary bases at NASCC. NALF Waldron provides support for pilot training operations (touch-and-go flight training) and previously contained a Skeet Range used for cadet and security personnel weapons training and qualification. NALF Waldron (851 acres in size) also had four 5,000-foot runways, of which only two (running north/south and northwest/southeast) are presently active and maintained. The Skeet Range was constructed in March 1945 and decommissioned sometime between June 1947 and July 1961. The former Skeet Range at NALF Waldron was comprised of three skeet firing arcs facing northward towards the installation fenceline, as well as "high" and "low" skeet houses located at the end of each arc.

The following sections provide general information about NALF Waldron, including its location and setting; a brief history of the installation; its missions over time; and a history of munitions-related training, storage, and usage.

Location and Setting

NALF Waldron is located in the far eastern side of Nueces County, Texas, and lies approximately three miles south of NASCC. NALF Waldron is situated on the southern end of the Encinal Peninsula and is bounded to the east by Waldron Road; the south by Yorktown Road; the west by Flour Bluff Road; and to the north by a fenceline separating the installation from a wooded area and a residential community.

The installation location is shown in Figure 10-2.1.

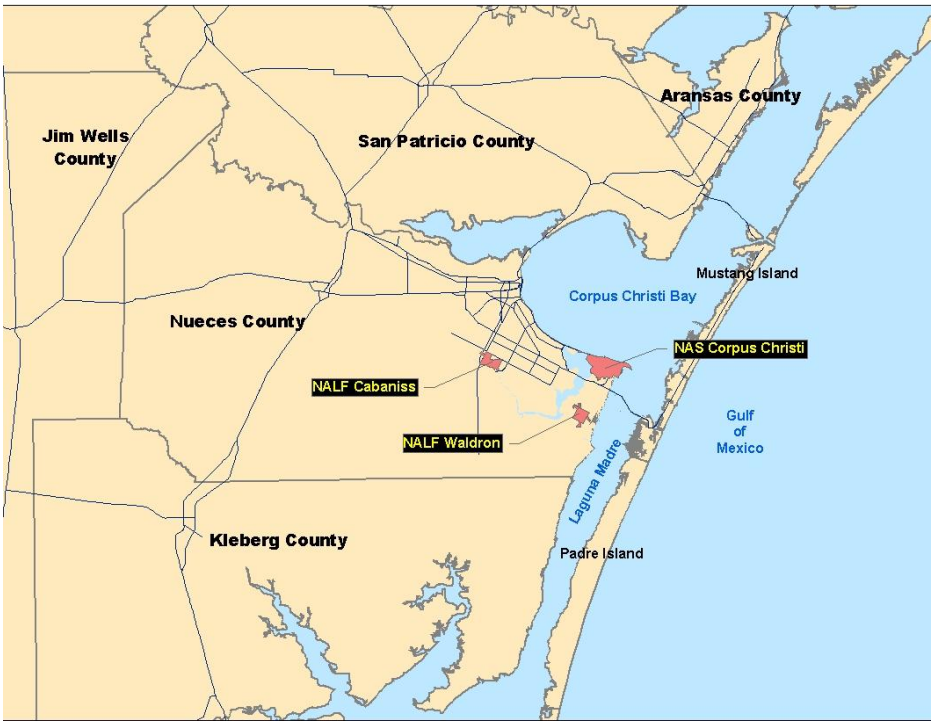


Figure 10-2.1: Installation Location

Installation History

Prior to the construction of NALF Waldron and NASCC, the northern tip of the Encinal Peninsula was undeveloped land primarily covered in scrub oak, mesquite, and large sand dunes. Several permanent residences and vacation homes were the only buildings present. In December 1938,

the Navy recommended the Flour Bluff area as a potential site for the construction of a new aviation training station due to the sparse population, favorable location, and the potential for year-round flight operations. Additionally, the City of Corpus Christi offered to donate the land required for the installation and compensate the 100 families and residents for relocation.

The installation received Congressional approval, and an appropriations bill was signed on June 13, 1940, authorizing construction of NASCC and 25 OLFs to support the main installation. Construction began June 30, 1940, and the installation was officially commissioned on March 12, 1941. Six of the OLFs were constructed as auxiliary bases, including (dates listed indicate date of commission):

- Naval Air Auxiliary Station (NAAS) Rodd Field, June 7, 1941 (primary flight training)
- NAAS Cabaniss Field, July 9, 1941 (intermediate flight training)
- NAAS Cuddihy Field, September 3, 1941 (intermediate flight training)
- NAS Kingsville, July 4, 1942 (advanced flight training for fighters and bombers)
- NAAS Waldron Field, April 1, 1943 (torpedo bombing aircraft flight training)
- NAAS Chase Field, June 1, 1943 (instrument flight training)

Each auxiliary station supported up to two squadrons at a time, separate from the squadrons based at the main installation. All auxiliary stations were outfitted with landing fields, runways, hangars, shops, barracks, mess halls, and recreational centers. With the main installation and the six auxiliary fields, NASCC became the Navy's largest air training center. The Navy also acquired tracts of land to the south of Corpus Christi and on Mustang Island to perform practice bombing and other military operations. Some bombing maneuvers also occurred in the bays surrounding the region. These former bombing ranges are currently being evaluated by the U.S. Army Corps of Engineers (USACE) as part of the Formerly Used Defense Site (FUDS) program.

Flight instruction at NASCC began on April 1, 1941. Cadets began their instruction with two weeks of basic training followed by four weeks of ground training and classroom instruction. Following this initial training, the cadets moved into a nine-week program of classroom and flight training on the N3N "Yellow Peril" trainer aircraft. Flight training was then broken down into specific divisions, including primary, basic, instrument, and advanced flight classes. Following completion of primary training, the more advanced aerial training was performed at the auxiliary fields.

With the December 1941 attack on Pearl Harbor, NASCC became a supply base for shore patrol units. The station served as a major point of defensive operations in the Gulf Coast area, conducting reconnaissance in the Gulf of Mexico for enemy ships, aircraft, and submarines. Flight training efforts were doubled from 300 cadets per month to 600 cadets per month by utilizing the auxiliary fields. By the conclusion of World War II (WWII), nearly 35,000 aviators had been trained at the installation.

Following the conclusion of the war, NASCC's mission was reduced to include only primary and instrument flight training.

As a result, NAAS Waldron was temporarily decommissioned (January 24, 1947) along with NAAS Cabaniss, NAS Kingsville, and NAAS Rodd. The Navy leased the installation to Nueces County under a Revocable Permit on July 17, 1947, with an air operations buildings (i.e., control tower). Nueces County terminated the Revocable Permit in October 1950, returning the property to the Navy. Touch-and-go flight training continued at the inactive installation; ultimately, the installation was redesignated as NALF Waldron in June 1969. NALF Waldron currently supports the training mission of NASCC by providing runways for touch-and-go landing training and other student training operations.

Table 10-2 summarizes the major events at NALF Waldron.

Munitions-Related Training / Storage / Usage

Station maps of NAAS Waldron from the 1940s indicate the presence of an ammunition locker located behind a hangar and a gunnery building next to the Skeet Range. The ammunition locker likely stored small arms ammunitions for the station aircraft and likely include .30 and .50 caliber munitions. The gunnery building likely stored shotgun ammunition for use at the Skeet Range. These structures are no longer present at the installation. No other ordnance or munitions were stored at NAAS Waldron. Due to the installation's sole focus as a training airfield, NALF Waldron does not currently use, store, or train with any type of ordnance or munitions. The NALF Waldron Skeet Range was the sole range identified by NASCC Environmental Division personnel in the MRP Navy Range Inventory. However, during the site visit and data review process, an additional range, the Fixed Gun Boresight Range, was identified at NALF Waldron. This range was once located in the southeast corner of the facility and was used to synchronize the fixed machine guns in aircraft wing mounts during WWII. The range was eventually abandoned and the site later used in the 1950s to 1970s as a landfill for the disposal of construction rubble and debris from Hurricane Celia (1970). The disposal area was investigated and sampled, and a

closure letter for the disposal area, including the former range, was granted from the state regulatory agency. As the site is considered closed, this former range will not be investigated as part of the MRP.

Information regarding the NALF Waldron Skeet Range is generally limited. No property records were found at NASCC for the buildings associated with these ranges. In addition, few records are available, or known to be available, describing the construction, use, and demolition of the range. Historical data provided no indication that ordnance or explosives were used or stored at the range, and the possibility is considered unlikely as the range utilized only small arms ammunition and the installation's primary mission was flight training.

Skeet Range

The former Skeet Range at NALF Waldron is an approximately 8.6-acre area located in the northeastern portion of the installation, 520 feet northeast of the intersection of Runway 31 (still active) and Runway 26 (abandoned but still visible). The range area is bounded on the south and west by Runway 31, and by grasses, shrubs, trees, and the installation fenceline to the east and north. Station drawings indicate the Skeet Range was constructed in March 1945 and was used for cadet and security personnel weaponry training and qualification, moving target orientation training of Naval aviators, and potentially recreation. Ammunition used at the site likely included 12-, 16-, and 20-gage and .410 caliber shotgun ammunition and possibly other small arms ammunition. Station drawings indicate the range was demolished sometime between June 1947 and July 1961. No records were found indicating the methods or the exact date of the range demolition; however, the installation POC indicated that the range was most likely brought to grade by bulldozing. The area where the Skeet Range was located is currently overgrown with vegetation, and there is no visual evidence of the former structures associated with the range (e.g., no ground scarring or concrete).

10-3 PHYSICAL AND ENVIRONMENTAL CHARACTERISTICS

The following sections provide general information for NALF Waldron including: its climate; topography; geology; soil and vegetation types; hydrology; hydrogeology; cultural and natural resources; and threatened, endangered, and protected species.

10-3.1 Climate

The climate at NASCC, including NALF Waldron, is a moderate to semi-tropical marine climate with hot, humid, breezy summers and mild winters. The wind direction is predominantly from the southeast during the warmer months and from the northwest and north during periods of higher pressure and cold fronts during cooler months. Average low and high temperatures are 42 degrees Fahrenheit (^{o}F) (January) and 86°F (July), respectively. The number of clear days averages 114 per year. Annually, there are more than 100 days of high temperatures of 90°F or higher and fewer than seven days of low temperatures at or below 32°F.

Cold fronts, periodic thunderstorms, and hurricanes generally have the greatest impact on rainfall, which averages 34 inches annually. Extremes in precipitation can occur, ranging from drought to torrential rains associated with tropical storms and hurricanes. Nine hurricanes have made landfall in the Corpus Christi Bay area since 1900. The hurricanes of 1919 and 1945 and Hurricane Celia (1970) caused widespread property damage at NASCC and the region. Storm surges associated with hurricanes and tropical storms can greatly affect the Corpus Christi Bay area. On average, a tropical storm or hurricane makes landfall in the Corpus Christi Bay area once every 10 years, with a major storm once every 30 years.

10-3.2 Topography

The general topography of the mainland areas of Nueces County around Corpus Christi Bay can be described as low-lying coastal area consisting of flat coastal prairies, chaparral pastures, and farmland. Elevations range between 15 and 22 feet above mean sea level. NALF Waldron is approximately 20-25 feet above mean sea level on very level terrain.

10-3.3 Geology

The coastal plain of the Corpus Christi area is underlain by Pleistocene river, delta, and shoreline sediments deposited during the interglacial periods. NASCC is underlain by the Beaumont Formation, characterized by barrier island and beach deposits composed of fine-grained sands. Numerous pimple mounds and poorly defined relic beach ridges characterize the land surface. Locally active sand dunes are present in undisturbed areas. The barrier island and beach deposits of the Beaumont Formation are typically less than 60 feet thick. Other stratigraphic units, in order of increasing age, include the Montgomery Formation, Lissie Formation, Willis Formation, and the Goliad Sand.

10-3.4 Soil and Vegetation Types

NALF Waldron is underlain by the Galveston-Mustang soil unit. Generally, these soils have a surface layer 10 inches thick or less, underlain by a three- to four-foot thick layer of fine-grained sand, followed by saturated fine white sand from four to 10 feet. The soils are typically moist in their lower layers. Common limitations of the area soils are the presence of a high water table, erosion hazard, flood hazard, saturated conditions, and high permeability.

Principle vegetation types at NALF Waldron were identified in the 2001 Integrated Natural Resources Management Plan (INRMP) for the installation. The predominant vegetation types are Live Oak-Redbay Woodlands. This community is globally rare and found only in the Coastal Bend of Texas. It is comprised of shrub thickets four to eight feet in height with various openings comprised of midgrasses and some tall trees with closed canopy. Coastal live oak is the dominant species, although the community includes a mix of laurel oak (Quercus hemisphaerica) and redbay (Persea borbonia). Vegetation species commonly found in this environment include Yaupon Holly (*Ilex Vomitoria*), American Beautyberry (*Callicarpa Americana*) , Greenbriar (*Smilax bona-nox*) and Wax-myrtle (*Myrica cerifera*). Drainage ditch areas on the southern end of the installation also include the Spikerush – Rush – Umbrella-Sedge, Seasonally Flooded Herbaceous Vegetation community, with a number of rare wetland species. Species found within this community include the one-head porcupine-sedge (*Fuirena scirpoidea*), spreading beakrush (*Rhynchospora divergens*), and smallseed beakrush (*Rhyncospora microcarpa*). Drainage ditches within the installation are not considered jurisdictional wetlands. Operational requirements and mission safety for NALF Waldron have created the need to maintain large portions of the installation as open grassland, including the area occupied by the former training complex. These areas are maintained through periodic mowing. Grass species may include the Kleberg bluestem (*Dicanthium annulatum*), silky bluestem (*D. sericeum*), and King Ranch bluestem (*Bothriochloa ischaemum* var. *songarica*).

The INRMP indicates that the Live Oak-Redbay Woodland community is considered an ecologically sensitive area because of its global rarity and potential for providing important habitat to migratory birds, mammals, amphibians, and reptiles. However, while this community at NALF Waldron is considered an ecologically sensitive area, the deep, sandy soils of the Encinal Peninsula are unlikely to support any plant species of federal concern.

10-3.5 Hydrology

Rainfall at NALF Waldron is collected in storm drains and open drainage canals near the runways, which ultimately slowly drain southwest toward Oso Bay (approximately 1.4 miles) or southeast toward Laguna Madre (approximately 0.9 miles). Water quality, monitored by the Texas Commission on Environmental Quality, in Oso Bay, Corpus Christi Bay, and Laguna Madre is good.

No natural lakes, rivers, or streams are present on the installation. There are no wetlands found at NALF Waldron. Permanent tidally-influenced surface water lagoons and a large tailings pond are present to the south of the installation. These surface water bodies may exist due to high tides, storm surge, or flooding from rain events.

10-3.6 Hydrogeology

The average depth to groundwater at NALF Waldron is six feet bgs. This shallow groundwater zone is subject to salt-water intrusion due to its close proximity to Laguna Madre and Oso Bay. The water table aquifer (6 to 250 feet bgs) is predominantly sandy material overlying a clay zone with low permeability. Regional groundwater flow in the Corpus Christi area is to the northeast; local flow paths at NALF Waldron are unknown. Artesian aquifers (250 to 2,800 feet bgs) underlying NALF Waldron are moderately to highly saline and, therefore, have limited potential use. Potable water for the installation is supplied from Lake Corpus Christi, 43 miles to the northwest.

10-3.7 Cultural and Natural Resources

No data sources describing archaeological, cultural, or natural resources were found for the NALF Waldron installation.

10-3.8 Endangered and Special Status Species

The 2001 INRMP provides a survey of the presence of rare, threatened, and endangered species, their relative abundance, and the locations of identified critical habitats at NALF Waldron. During the study, plant, herpetofauna, bird, and mammalian surveys were completed. The surveys included all state or federally listed species, as well as those species that are candidates for listing.

The surveys conducted at NALF Waldron did not indicate occurrences of threatened or endangered species. However, the potential exists for migratory species to move into suitable habitats within the installation. In particular, the Live Oak-Redbay Woodlands community at NALF Waldron serves as a resource (shelter, food, and resting points) for migratory bird populations.

The maritime pocket gopher (Geomys personatus maritiums), a species of concern, may be the most significant species for wildlife management and protection at NALF Waldron. The species, which is also found at the main installation, is under consideration for listing as a threatened species. Gopher populations are noted throughout the installation by the fan-shaped mounds created by tunneling. A number of mounds have been identified in the southeast and southwest corners of NALF Waldron.

While not documented during the most recent survey, the INRMP indicates that the protected species listed in Table 10-3 have the potential to inhabit NALF Waldron.

TABLE 10-1

**SUMMARY OF OTHER THAN OPERATIONAL RANGES
NALF WALDRON
NAS CORPUS CHRISTI, TEXAS**

Site Name	NORM Site No.	Size (acres)	Use	Dates of Use
Skeet Range	SKR	8.6	Skeet Range	1945 – Unknown[1]

1 – The original skeet range was constructed in 1945 and covered approximately 8.6 acres. The range was demolished sometime between June 1947 and July 1961.

TABLE 10-2

TIMELINE OF SIGNIFICANT EVENTS
NALF WALDRON
CORPUS CHRISTI, TEXAS

Time Period	Significant Event
1940	• Construction of NASCC and 25 OLFs was authorized. • Six OLFs were constructed as auxiliary bases.
1940 - 1941	• NASCC was constructed and commissioned. • Attack on Pearl Harbor caused surge of training at NASCC. • NASCC became a supply base and major point of defensive operations in the Gulf Coast area.
1943	• NAAS Waldron Field was constructed and commissioned for torpedo bombing aircraft flight training.
1947	• NAAS Waldron Field disestablished and leased to Nueces County.
1950	• Nueces County terminates Revocable Permit, returning installation to U.S. Navy. NAAS Waldron Field moved to inactive status.
1969	• NAAS Waldron Field redesignated as NALF Waldron.

TABLE 10-3

SUMMARY OF KNOWN OR POTENTIAL PROTECTED SPECIES
NALF WALDRON
CORPUS CHRISTI, TEXAS

Ecological Receptors	Species
Federal Endangered	• None Reported
Federal Threatened	• None Reported
State Endangered	• None Reported
State Threatened	• Texas Botteri's Sparrow • Black-Spotted Newt • Sheep Frog • South Texas Siren –large form • Scarlet Snake • Texas Indigo Snake • Texas Tortoise • Texas Horned Lizard
Other Ecological Receptors	• Maritime Pocket Gopher (species of concern) • Common flora/fauna such as large mammals (e.g. deer) • Small mammals • Reptiles/amphibians • Migratory and indigenous birds • Grassland birds

INDIVIDUAL MRP SITE-SPECIFIC CHARACTERISTICS/PROBLEM DEFINITIONS

The following sections provide site-specific information about each of the sites located on NALF Waldron, including history and site description; land use; access controls and restrictions; visual survey observation and results; contaminant migration routes; and receptors.

SAP WORKSHEET #10. 1:
PROBLEM DEFINITION/CONCEPTUAL SITE MODEL FOR THE SKEET RANGE

10.1 THE SKEET RANGE

10.1.1 History and Site Description

The Skeet Range was located on the easternmost side of NALF Waldron. The area is northeast of the currently operational Runway 31, south of the installation's northern boundary fenceline separating the installation from residential neighborhoods, and 750-feet west of the installation boundary and Waldron Road.

The Skeet Range was constructed in 1945 and occupied approximately 8.6 acres. The range was composed of three skeet firing arcs facing to the northwest, situated end-to-end. Each firing arc contained a "high" skeet house on the left side of the arc, a "low" skeet house on the right side. The range also contained a gunnery building, east of the skeet arcs, that may have housed ammunitions for use at the Skeet Range. The Skeet Range was used for cadet and security personnel weaponry training and qualification, moving target orientation training of Naval aviators and, possibly, for recreation. Munitions use was limited to small arms, primarily shotguns (12-, 16-, and 20-gage and .410 caliber ammunition).

According to Army Technical Manuals (referenced as AR 750-10 and TM 9-855) and the Navy Programming Guide (1958), each firing arc was laid out as a 63-foot radius semi-circle with concrete walkways and five firing points. The surface danger zone (SDZ) for each firing arc (which includes the down range hazard area and safety fan) consisted of a semi-circle with a 900-foot radius that utilized the same apex as the shooting field. During operation of the range, the SDZ for each firing arc would be combined, with a total acreage of approximately 37 acres.

The site boundary for the Skeet Range, which includes approximately 8.6 acres, encompasses the firing arc, target area, and impact area where the lead shot and broken clay targets would be found (also known as the maximum shotfall zone). The SDZ is the portion of the former range that represented the area where the weapons, when fired from the firing arc, could endanger

personnel. The SDZ was used to define the area between the firing arc and target area, the impact area, the ricochet trajectory area, and the secondary danger area. Operation of the Skeet Range as a training facility ceased at an unknown date. Station drawings indicate the range was demolished sometime between June 1947 and July 1961. Range demolition is confirmed by an aerial photograph of NALF Waldron taken in October 1967, which indicates the Skeet Range was no longer present. The method of demolition is unknown; however, the installation POC indicated that the range was likely brought to grade by bulldozing.

Topography

The Skeet Range is between 20 and 25 feet above sea level. The range is mainly flat, with a slight slope to the northeast. General topographic data for the NALF Waldron installation is provided in Section 10-3.2.

Geology

Site-specific geological information for the Skeet Range is not available. Regional geologic information is provided in Section 10-3.3.

Soil and Vegetation Type

The soil at the former Skeet Range has been characterized as the Galveston-Mustang soil unit. The soil is sandy, well drained, and highly permeable, as described in Section 10-3.4.

Vegetation in the area of the former Skeet Range consists primarily of tall grasses, shrubs, and some trees. Areas containing low-growing grasses between the Skeet Range and runway 31 are mowed periodically. The former Skeet Range is part of the Live Oak–Redbay Woodland community, an ecologically sensitive area, which is found directly west, north and east of the range. General vegetation data for the NALF Waldron installation is described in Section 10-3.4.

Hydrology

No natural lakes, rivers, or streams are present on the Skeet Range. There are no wetlands located within the boundaries of the Skeet Range. General hydrological data for the NASCC installation is provided in Section 10-3.5.

Hydrogeology

Groundwater monitoring wells have not been installed within the boundaries of the Skeet Range. Groundwater may be present approximately 6 feet bgs in the area of the Skeet Range. The groundwater flow direction is west toward Oso Bay. Regional groundwater information is provided in Section 10-3.6.

Cultural and Natural Resources

No data sources describing archaeological, cultural, or natural resources were found for the NALF Waldron installation.

Endangered and Special Status Species

The surveys conducted at NALF Waldron did not indicate occurrences of threatened or endangered species. However, the potential exists for migratory species to move into suitable habitats within the installation. In particular, the Live Oak-Redbay Woodlands community at NALF Waldron serves as a resource (shelter, food, and resting points) for migratory bird populations.

The maritime pocket gopher (Geomys personatus maritiums), a species of concern, may be the most significant species for wildlife management and protection at NALF Waldron. The species, which is also found at the main installation, is under consideration for listing as a threatened species. Gopher populations are noted throughout the installation by the fan-shaped mounds created by tunneling. A number of mounds have been identified in the southeast and southwest corners of NALF Waldron.

10.1.2 Visual Survey Observations and Results

A site walk of the NALF Waldron Skeet Range was conducted by the Malcolm Pirnie data collection team (Ms. Nelline Scheuer and Mr. Mike Madl) and UXO Technicians (Mr. Dan Hains and Mr. Lee Nolan) on July 29, 2003. During the site walk, the following conditions were noted:

- The former Skeet Range was demolished and no buildings were present.
- The Skeet Range was overgrown with grasses (six inches to five feet) and shrub thickets (up to eight feet).
- There was no evidence of flooding or erosion.

- There was no visual evidence of the former structures or foundations associated with the range (e.g., firing arcs, skeet house foundations, gunnery building).
- There was no visual evidence of scarring on trees or shrubs in the vicinity of the range.
- A single .50 caliber cartridge was observed; no lead or clay pigeon fragments were observed.
- No physical evidence of MEC was observed.

The visual survey was performed by attempting to walk the perimeter of the range, followed by a transect across the center of the range. However, as the exact limits of the range were unknown at the time of the visual survey (no visual landmarks such as old skeet house foundations), the data collection team attempted to estimate the location of the former firing arcs based on a historical map and focused the perimeter walk around the estimated location. The transect was then walked across the center of the perimeter walk in order to focus the survey on the area with the highest likelihood of finding evidence of shot residue. The visual survey for the Skeet Range resulted in approximately 10 percent walked coverage and approximately 70 percent visual coverage of the former range.

No physical evidence of MEC was observed during the visual survey. Non-UXO items such as wood, metal, or concrete debris associated with the former range were not observed during the site walk. Clay target fragments associated with the former Skeet Range were not observed. The land is not currently used for operational purposes.

A single discharged .50 caliber cartridge was found at the former Skeet Range. While considered small arms ammunition, the presence of a .50 caliber cartridge is not consistent with the known uses of the Skeet Range; typically only shotguns were used for training at this range. However, the .50 caliber cartridge may have originated from past operations at the installation, as aircraft stationed at NALF Waldron during WWII utilized this type of small arms ammunition in their wing-mounted machineguns and a Fixed Gun Boresight Range was once utilized in the southeastern corner of the installation. While it is not known how this cartridge was deposited at the Skeet Range, it may have been expended or dropped at another location at the installation and was subsequently moved by various means (station personnel or mowing activities may have moved the item).

A visual depiction of the site reconnaissance is provided on Map 10.1-1 located at the end of Section 10.1. Additional range/site details are illustrated on Map 10.1-2, also located at the end of Section 10.1.

10.1.3 Munitions and Munitions-Related Materials Associated with the Site

No MEC was observed at the range during the visual survey. Based on the known uses of small arms ranges, only small arms ammunition (12-, 16-, and 20-gage and .410 caliber shotgun and potentially other small arms ammunition) would be expected to be used at the Skeet Range. No other ordnance, explosives, or weapons are expected to have been used or stored at the site. Based on the information obtained during the data collection process (interviews, records search, etc.), no special consideration munitions are known or suspected to have been used at the site. Therefore, the Skeet Range is not suspected to contain chemical warfare material filled munitions, electrically fuzed munitions, or depleted uranium associated munitions.

10.1.4 MEC Presence

The entire site has been subdivided and categorized into one of three levels of MEC presence including: known MEC areas, suspect MEC areas, and areas where no evidence exists to indicate that MEC are known or are suspected to be at the site. The MEC presence is discussed below.

Map 10.1-3 illustrates the munitions characterization of the Skeet Range and is provided at the end of Section 10.1.

Known MEC Areas

Because the site was used only for small arms training and there is not historical, visual, or known evidence of explosives used at the site, there is no evidence of MEC. As such, there are no known MEC areas associated with the Skeet Range.

Suspected MEC Areas

As only small arms ammunition was used at the site, there are no suspected MEC areas associated with the Skeet Range.

Areas Not Suspected to Contain MEC

Based on observations made and data collected during the PA process, the 8.6-acre site, as well as the SDZ associated with the Skeet Range, is not suspected to contain MEC.

10.1.5 Ordnance Penetration Estimates

By design, skeet ammunition is dispersed as pellets over a small area in the direction of fire. According to the Navy Programming Guide (1958), the minimum SDZ for a skeet range is 900 feet. Pellets dispersed from a shotgun would be deposited on the ground surface well within this zone. The majority of the lead pellets would concentrate in the maximum shotfall zone between 375 and 600 feet from the firing point. Lead or clay target fragments would accumulate on the surface and would not penetrate the ground surface unless disturbed. Grounds maintenance operations in the area could have redeposited lead and clay target fragments in surface soils to a depth of two foot bgs.

10.1.6 Munitions Constituents

The primary MC of concern associated with shotgun ammunition is lead. Metallic lead is insoluble in water, but in the geochemical environment of most ranges it may slowly convert to other oxidized forms. Depending on the environment (e.g., soil characteristics, pH, and organic matter present), oxidation products can become mobile. However, lead mobility is effectively controlled by adsorption under the majority of conditions found on skeet ranges. In general, an exponential decline in lead concentrations has been observed in very short vertical distances due to adsorption or exchange reactions with clays, metal oxides, or organic mater in the soil. As such, lead mobility is not likely to be an issue at most ranges. However, while lead is not typically mobile in most environments, it is possible that limited migration of lead has occurred from the Skeet Range to other media (e.g., subsurface soil and groundwater), based on the permeable nature of the sandy soil at the site.

Other MC may include antimony, arsenic, copper, nickel, zinc, and constituents associated with black or smokeless powder (lead styphnate and lead azide). However, these constituents are less likely to be of concern since they are either present in the shotgun ammunition in only minor amounts/concentrations or are typically consumed when the shotgun round is fired. Polycyclic aromatic hydrocarbons (PAHs) associated with the usage of clay targets may also be present at the site. However, PAHs present in clay targets tend to be tightly bound in the petroleum pitch and limestone matrix of the target and are not readily available to the environment. In addition, the clay targets contain low solubility, high molecular weight PAHs that are not likely to effectively leach into the surrounding soils. However, as is the case with lead, PAHs and other MC may have migrated from the Skeet Range to other media in a limited fashion based on the permeable nature of the surface soil at the site.

The majority of the lead pellets discharged at the Skeet Range would accumulate in the maximum shotfall zone between 375 and 600 feet from the firing arc. This zone is one of two areas in which MC, if present, would be concentrated. The other location is the range floor directly in front of the firing positions. MC accumulates in this area from shotgun muzzle discharge at each firing position and from clay target fragments. MC accumulation would likely be found in the upper six inches of surface soil within these two primary concentration areas. However, any near-surface disturbances such as periodic mowing or range demolition/regrading could redistribute MC to depths of two feet.

No sources of information were found which might indicate whether soil or groundwater sampling had been performed at the former Skeet Range to confirm the presence of MC in surface soil. However, based on the known historical use of the former Skeet Range for moving target orientation training and the nature of the MC commonly associated with small arms ammunition and clay targets, MC is suspected to be present in surface soil at the Skeet Range

10.1.7 Contaminant Migration Routes

MC, if present at the Skeet Range, would be found primarily in the near-surface soils. Grounds maintenance activities (mowing) and any range demolition activities (bulldozing) may have resulted in the deposition of lead pellets and clay target fragments in the top one foot of surface soil at the site. Migration of MC across the range and to adjacent areas may occur naturally through surface soil erosion (particularly during intense precipitation and storm events), plant/animal uptake, or by human activities, including maintenance (e.g., mowing and vegetation removal). The dense grasses, shrubs, and other existing vegetation at the range likely act as a cover on top of the MC, limiting lateral migration by wind or surface runoff. The chemical and physical properties of soils affect the permeability and downward migration of chemical constituents.

MC could also potentially leach into subsurface soil and the shallow groundwater beneath the range due to the permeable nature of the sandy soil at the site. The soils at the Skeet Range are sandy, have low water capacity, and are highly permeable. These soil conditions may increase the rate at which chemical constituents could migrate downward to the water table. However, despite these favorable conditions for increased downward migration, the chemical and physical nature of the MC most likely to be present at the range (e.g., low solubilities and high adsorption potential of metals and PAHs) likely limits the migration. Once present in groundwater, MC could potentially migrate with the groundwater flow. However, based on the chemical and physical nature of the MC most likely to be present at the ranges (e.g., metals, PAHs), it is unlikely that

contamination would migrate to groundwater, discharge to surface water, and subsequently be available to receptors. Additionally, the shallow groundwater zone in the area is moderately to highly saline and has limited potential use (potable water is provided from Lake Corpus Christi 43 miles to the northwest).

While drainage structures are present to carry surface runoff southwest toward Oso Bay (1.4 miles) or southeast toward Laguna Madre (0.9 miles), none are located on the Skeet Range and there is little potential for MC to be carried so far from the former range and installation and deposited into these surface water bodies. The nearly level terrain at the Skeet Range also limits the potential for erosion and subsequent MC migration by surface runoff to nearby surface water bodies.

10.1.8 Receptors

There are two groups of potential human receptors and two groups of potential biota receptors potentially present at the Skeet Range. The first group of current potential human receptors includes Navy personnel, such as security personnel patrolling near the area of the former range and Public Works personnel conducting environmental or ecological surveys. The second group of potential human receptors includes contractors performing grounds maintenance (mowing and vegetation removal) on the former range area that could also be exposed to MC. Visitors are not considered potential human receptors as the site is located within the flightline control area (thereby restricting access), there are no structures or equipment present, and there is no specific reason for visitors to be present at the former range. Hunters are not considered potential human receptors as hunting is not permitted on the installation. In addition, trespassers are not considered potential receptors, as the installation is fenced and periodically patrolled, the former Skeet Range is covered in vegetation, and there is nothing of particular interest at the site.

The close proximity of the former Skeet Range to both an active runway and residential neighborhoods likely precludes the construction of new facilities and places restrictions on new or existing operations. Also, land use is expected to remain as a Navy installation for the foreseeable future. Thus, development is unlikely in the future. Therefore, all current potential receptors are also considered potential future receptors.

Current and future biota receptors include the current flora (predominantly grassland species) and fauna (large mammals such as deer, small mammals such as rabbits and the burrowing maritime pocket gopher, reptiles/amphibians, and bird species) present at the site. The various media through which the potential receptors may be exposed to MC are listed in the CSM.

Nearby Populations

Local and installation populations are as described in Section 10.1.8.

The former Skeet Range is located in the northeastern corner of the installation, approximately 520 feet northeast of Runway 31 (currently still active). The site is located in an uninhabited area of the installation, with only security patrols occurring in the area. The installation has no military residences. A residential neighborhood is present beyond the installation's northeast boundary, approximately 450 feet to the north and 850 feet to the east of the former range.

Buildings Near/Within Site

There are currently no buildings or structures at the former Skeet Range. The nearest structure is Runway 31, aligned in the northwest to southeasterly direction, and south and west of the former range. The air control tower for the operational runways is located 2,000 feet to the southwest. There are also recreational fields located to the east and southeast of the installation, approximately 2,300 feet in distance. Residential homes are present approximately 450 feet north and 850 feet east of the former Skeet Range.

Utilities On/Near Site

A limited review of GIS files describing utilities located at NALF Waldron, revealed there are no electric, gas, water, sewer, or other utilities on the Skeet Range.

10.1.9 Land Use

The Skeet Range is closed and has been demolished. The area where the Skeet Range was located is currently overgrown with vegetation and there is no visual evidence of the former structures associated with the range (e.g., no ground scarring or concrete). Residential areas are present north and east of the former Skeet Range. Land use in the area is designated as open space; however, the extent of the Skeet Range falls within the flightline control area. As the former range lies adjacent to an active runway and within flightline control, future use is not expected to change. Vegetation (grasses) in the areas to the west and south of the range is maintained through periodic mowing. The majority of the land use at NALF Waldron is in support of primary and intermediate flight training under CNATRA. Thus, development on the former Skeet Range is unlikely in the future.

10.1.10 Access Controls / Restrictions

NALF Waldron is a fenced installation, with a locked gate present on the eastern side of the installation. Security personnel are not regularly posted at the entrance to the installation. There is no patrol road present around the installation perimeter. The Skeet Range is fully contained within NALF Waldron; it is not separately enclosed or bounded. The installation fenceline is 400 feet north and 750 feet east of the range, and remains in good condition.

The former Skeet Range is located within the flightline control area of NALF Waldron. The few visitors to areas within the flightline control areas require escorts and approval from Air Operations. However, the only operation typically performed in the area of the former Skeet Range is periodic mowing.

10.1.11 Conceptual Site Model

This CSM was developed following guidance documents issued by the USEPA for hazardous waste sites and the USACE for ordnance and explosives (OE) sites. Guidance documents included the USEPA's Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA (EPA/540/G-89/004) and the USACE CSM Guidance Development of Integrated Conceptual Site Models for Environmental Ordnance and Explosives (OE) Sites, which was final as of February 2003.

The CSM describes the site and its environmental setting. The CSM presents information regarding: 1) MEC and/or MC known or suspected to be at the site; 2) current and future reasonably anticipated or proposed uses of the real property; and 3) actual, potentially complete, or incomplete exposure pathways that link them. The CSM is the basis for the risk evaluation, prioritization, and remediation cost estimate.

A key element of the CSM is the exposure pathway analysis. For MEC, a complete or potentially complete exposure pathway must include the following components: 1) a source (e.g., locations where MEC are expected to be found); 2) access (e.g., controlled or uncontrolled access, items on the surface or within the subsurface); 3) an activity (e.g., non-intrusive grounds maintenance or intrusive construction); and 4) receptors (e.g., Navy personnel, construction workers, recreational users or authorized visitors). It is important to recognize that environmental mechanisms (e.g., erosion) and/or human intervention may result in the repositioning of MEC.

For MC, a complete or potentially complete exposure pathway must include the following components: 1) a source (e.g., locations where MC are expected to be found); 2) an exposure medium (e.g., surface soil); 3) an exposure route (e.g., dermal contact); and 4) receptors (e.g., Navy personnel, construction workers, recreational users or authorized visitors). If the point of exposure is not at the same location as the source, the pathway may also include a release mechanism (e.g., volatilization) and a transport medium (e.g., air).

The potential interactions between the source and receptors are assessed differently between MEC and MC. For MC, interaction between the source and receptors involves a release mechanism for the MC, an exposure medium that contains the MC, and an exposure route that places the receptor into contact with the contaminated medium. For MEC, interaction between the potential receptors and an MEC source has two components. The receptor must have access to the source and must engage in some activity that results in contact with individual MEC items within the source area.

Historical and visual evidence indicate that MEC are not present at the site; therefore, there are no exposure pathways for MEC. As such, an Exposure Pathway Analysis Figure for MEC was not created.

Several exposure pathways for MC are potentially complete for various media at the Skeet Range, as illustrated in Figure 10.1-2. Each potential source media is described below.

Surface Soil

MC may be present in surface soil due to the direct deposition of lead shot on the range floor. MC may also have been redistributed across the range due to the demolition of the range area. The possible demolition and regrading of the range may have buried MC to depths of two feet. In addition, the entire range area is currently covered by vegetation including grasses, shrub thickets, and some trees. Therefore, any remaining MC essentially would be covered by a “cap” of surface soil and vegetation, making the constituents inaccessible to human or wildlife receptors. These constituents are typically not mobile in the environment due to their physical and chemical properties (e.g., high sorption potential and low solubility under most environmental conditions) and likely have not migrated significantly from the site. Erosion and subsequent surface runoff of MC to adjacent areas is not expected due to the vegetative cover and flat topography of the former range. Thus, dermal contact, ingestion, and inhalation exposures to MC in surface soil are not anticipated. However, while not currently anticipated, any future movement

or grading of surface soils could make MC available for wind distribution and subsequent inhalation (e.g., dust) or direct contact.

Lead and PAHs are not readily absorbed and bioaccumulated by terrestrial plants and wildlife. Therefore, exposure of MC to ecological receptors via biological uptake is considered incomplete. In addition, hunting is not permitted at NALF Waldron; therefore, food chain exposures to humans are also considered incomplete.

Subsurface Soil

Subsurface soil may represent another exposure medium for MC; however, anticipated future land use is not expected to change due to proximity to an active runway, and sufficient evidence for a complete exposure pathway (i.e., construction workers exposed to subsurface soil by digging or earth moving operations) does not exist at this time.

Surface Water and Sediment

Due to the flat topography, infiltration is likely to be the predominant transportation mechanism for MC rather than surface runoff. While surface runoff generated from intense rain events could carry MC to previously unaffected areas near the range, runoff containing MC is not likely to reach Oso Bay or Laguna Madre due to vegetative cover, flat terrain and distance from the Skeet Range. Therefore, no route of exposure exists for either human or ecological receptors to surface water and sediment.

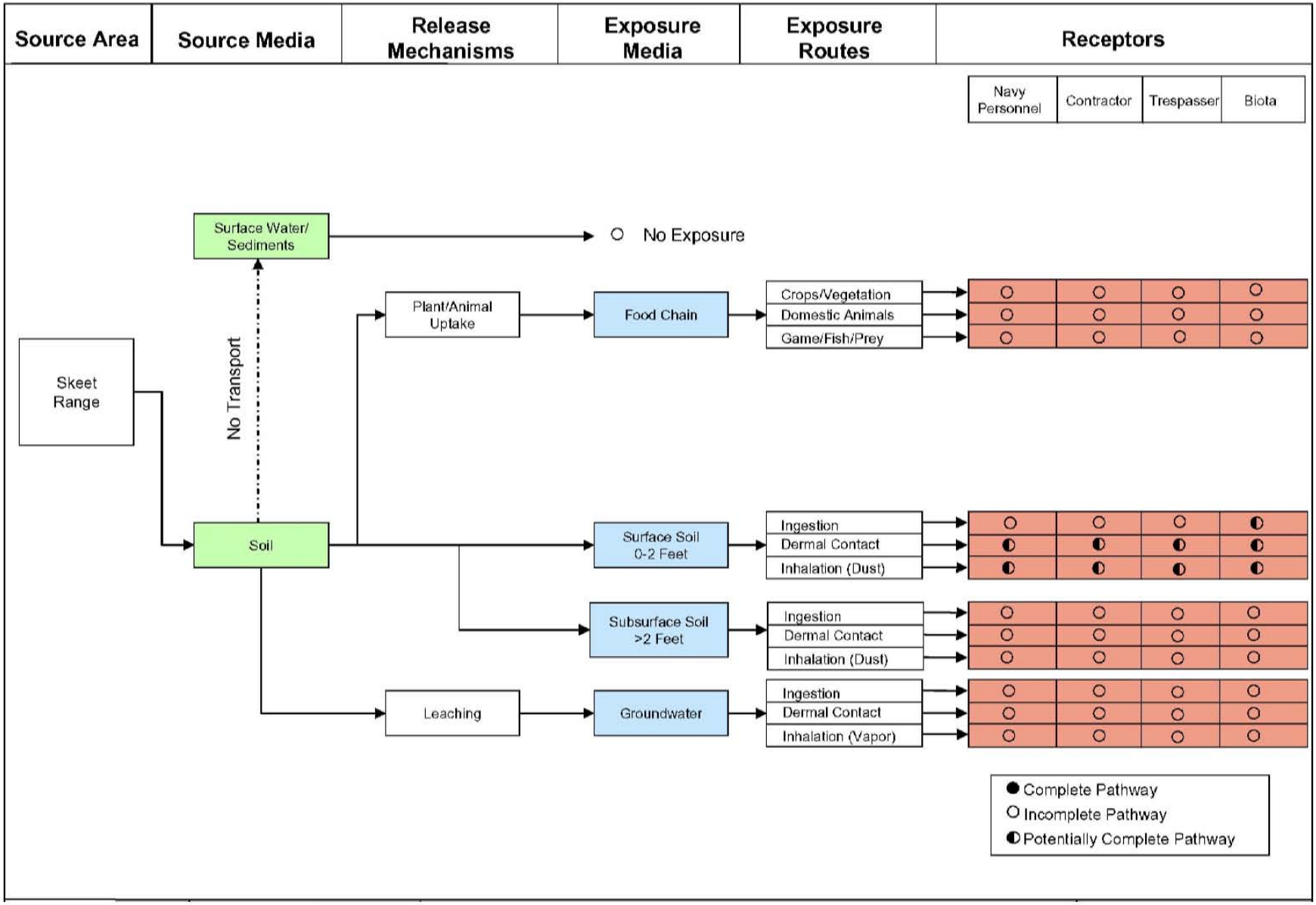
Groundwater

Leaching of MC into groundwater is possible due to the permeable sandy soil present at the Skeet Range. Though the local groundwater flow paths at the Skeet Range are unknown, groundwater will eventually discharge in either Oso Bay to the west or Laguna Madre to the east, both of which contain ecological and human receptors. However, based on the nature of the MC most likely to be present at the range (e.g., lead, PAHs) and the distance to the surface water bodies, it is unlikely that MC would migrate to groundwater, discharge to surface water, and subsequently be available to receptors at high concentrations. Additionally, there are no known users of the shallow groundwater in the area adjacent to the range. The major source of drinking water at NALF Waldron is supplied by Lake Corpus Christi, 43 miles to the northwest. Therefore, groundwater exposure pathways are considered to be incomplete.

A graphical illustration of the details of the CSM is included in Figure 10.1-3 at the end of this section. As shown on the illustration, the former Skeet Range was oriented for firing in a northerly direction. MC associated with the range was likely deposited on surface soil within the red range boundary, although lead shot fired from a shotgun had the potential to travel a full 900 feet to the edge of the SDZ. Demolition of the range may have redistributed MC within surface soil at the site. As shown on the illustration, the flat topography and vegetation present on range likely limited surface runoff to a slow northward migration and likely did not carry MC far from the site. Infiltration of MC through the permeable sands comprising the upper soil layer was likely the primary mode of contaminant transport. MC likely migrated into subsurface soil and groundwater via this process. However, as the shallow groundwater beneath the site is not used for potable supply and there is no foreseeable change in land use at the site (i.e., no activities which will disturb subsurface soil), mobilization of MC to subsurface soil and groundwater is not a concern.

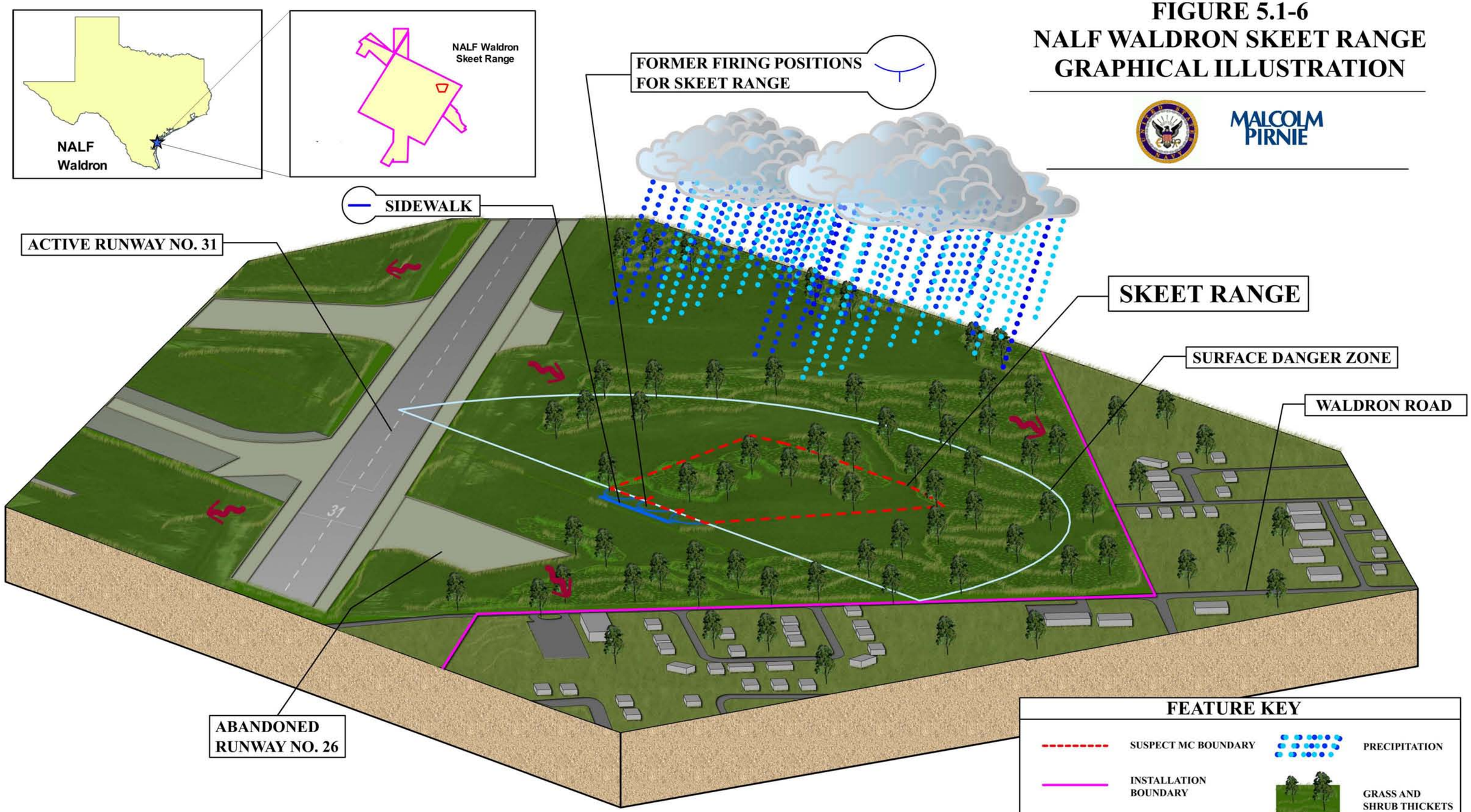
10.1.12 Problem Definition Summary

Based upon the information presented in this report, the Skeet Range was used for small arms qualification training of installation personnel, moving target orientation for Naval aviators, and likely for recreational purposes. Historical documentation (station documents and drawings) and NASCC personnel indicated that no other explosives or munitions were used at the site, and that the site was not used for any other purpose. There is no evidence of MEC at the Skeet Range. Based on historical operations at the site, it is possible for MC (lead, antimony, arsenic, copper, nickel, zinc, black powder, and PAHs) to exist in surface soil at the Skeet Range. The range was leveled between 1947 and 1961, and the area is currently not used for military purposes. Future use is not expected to change.



DRAWN BY GS	DATE 10/31/08	SKEET RANGE – MC EXPOSURE PATHWAY ANALYSIS	PROJECT NO. 112G01514
CHECKED BY LB	DATE 1/29/07		CTO NO. 0115
REVISED BY	DATE	NALF WALDRON, CORPUS CHRISTI, TEXAS	APPROVED BY / DATE
SCALE NOT APPLICABLE			DRAWING NO. FIGURE 10.1–2 / REV. 0

FIGURE 5.1-6
NALF WALDRON SKEET RANGE GRAPHICAL ILLUSTRATION

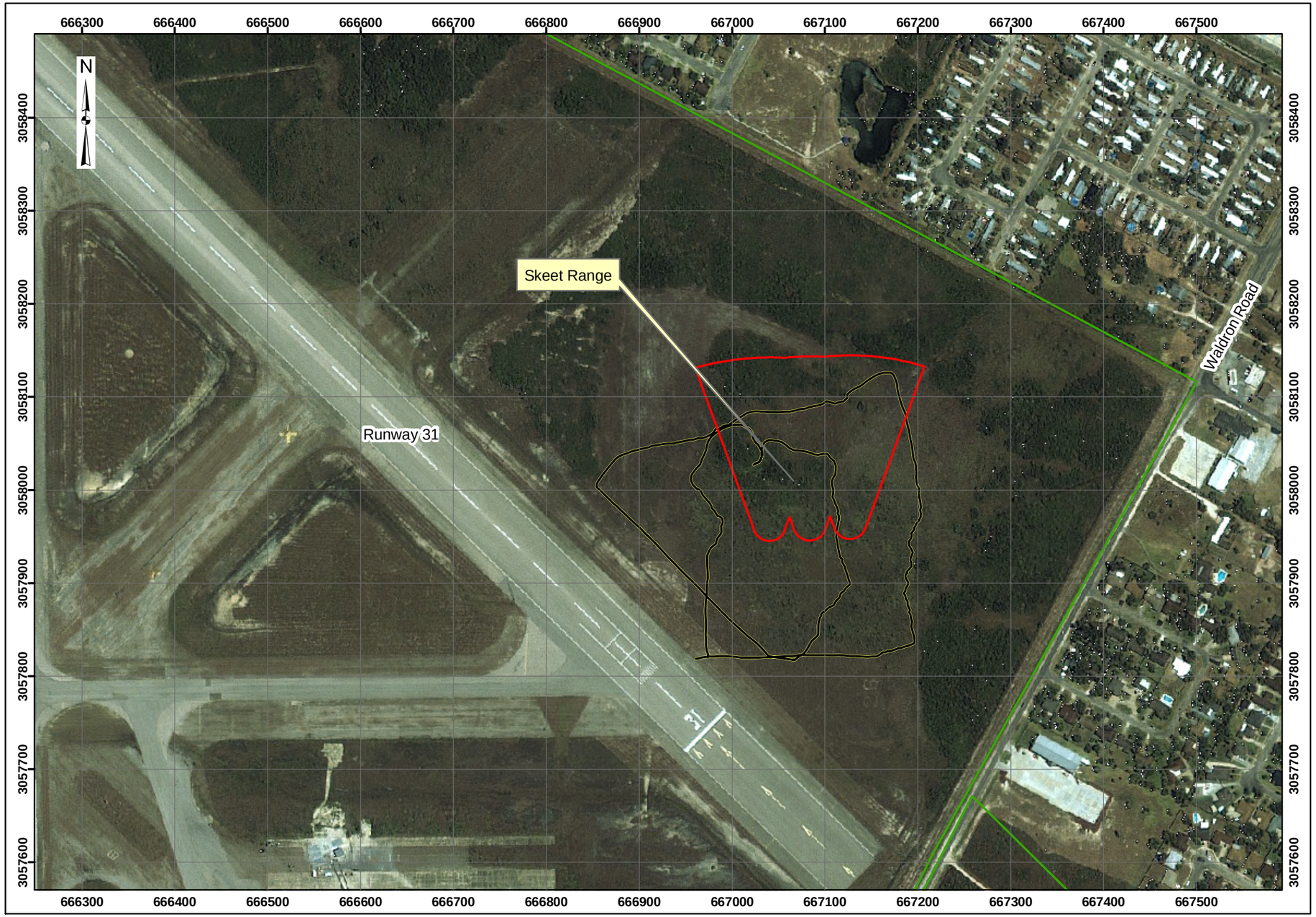


DISCLAIMER

THIS ILLUSTRATION IS INTENDED FOR USE IN CONJUNCTION WITH THE REPORT IN WHICH IT WAS SUBMITTED AND IS NOT INTENDED TO BE USED AS A STAND ALONE DOCUMENT.

NOTE:

1. THE SURFACE DANGER ZONE REPRESENTS THE FULL DISTANCE THAT A SHOTGUN DISCHARGE CAN TRAVEL (FOR A SKEET RANGE).



Preliminary Assessment
NALF Waldron, Texas

Map 10.1-1
Visual Survey
NALF Waldron Skeet Range

Legend

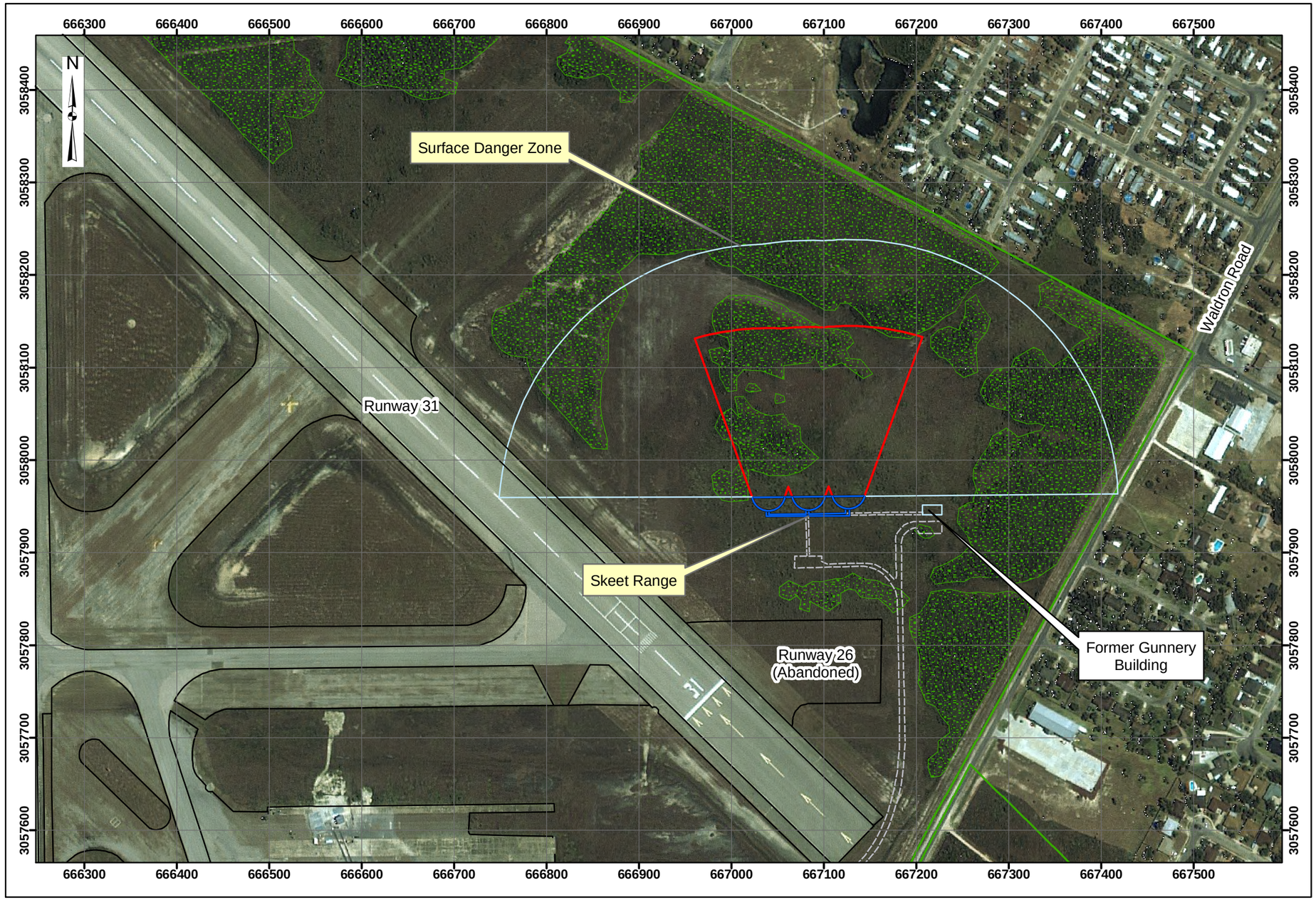
- Installation Boundary
- Skeet Range
- Site Reconnaissance

80 40 0 80 160 240 Meters

Data Source: Orthophoto, NAS Corpus Christi, TX, 2000
NAS Corpus Christi GIS/CAD Data

Coordinate System: UTM Zone 14
Datum: NAD 1983
Units: Meters

Contract: N62472-02-D-1300
Edition: Final Preliminary Assessment Report
Date: April 2005



Preliminary Assessment
NALF Waldron, Texas

Map 10.1-2
Range/Site Details
NALF Waldron Skeet Range

Legend

- Installation Boundary
- Former Firing Line
- Skeet Range
- Former Range Features
- Former Access Road
- Live Oak-Redbay Habitat
- Airfield

60 30 0 60 120 180 Meters

Data Source: Orthophoto, NAS Corpus Christi, TX, 2000
NAS Corpus Christi GIS/CAD Data

Coordinate System: UTM Zone 14
Datum: NAD 1983
Units: Meters

Contract: N62472-02-D-1300
Edition: Final Preliminary Assessment Report
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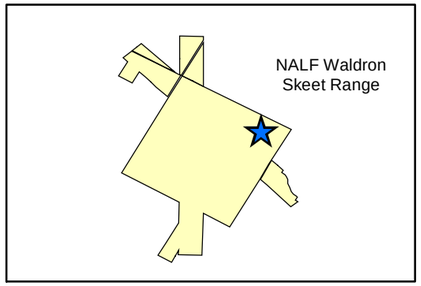

Preliminary Assessment
NALF Waldron, Texas

MALCOLM PIRNIE

Map 10.1-3
Munitions Characterization
NALF Waldron Skeet Range

Legend

Installation Boundary

Skeet Range

MEC Presence*

Known

Suspect

*There is no evidence of MEC as determined through historical documentation, interview, and visual survey.

Visual observations and/or historical documentation indicate that MC may be present at the site, but MC has not been confirmed by sampling or other means.

60 30 0 60 120 180 Meters

Data Source: Orthophoto, NAS Corpus Christi, TX, 2000
NAS Corpus Christi GIS/CAD Data

Coordinate System: UTM Zone 14
Datum: NAD 1983
Units: Meters

Contract: N62472-02-D-1300
Edition: Final Preliminary Assessment Report
Date: April 2005

APPENDIX B

STANDARD OPERATING PROCEDURES

APPENDIX B

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STANDARD OPERATING PROCEDURE
SOP-01

SAMPLE LABELING

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes the procedures to be used for labeling sample containers. Sample labels are used to document the sample ID, date, time, analysis to be performed, preservative, matrix, sampler, and the analytical laboratory. A sample label will be attached to each sample container.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Writing utensil (preferably black pen with indelible ink)
Disposable medical-grade gloves (e.g. latex, nitrile)
Sample log sheets
Required sample containers: All sample containers for analysis by fix-based laboratories will be supplied and deemed certified clean by the laboratory.
Preprinted sample labels
Chain-of-custody records
Sealable polyethylene bags
Heavy-duty cooler
Ice

3.0 PROCEDURES

3.1 The following information will be electronically printed on each sample label prior to mobilizing for field activities. Additional “generic” labels will also be printed prior to mobilization to be used for field QC and backups.

- Project number (CTO 0115)
- Sample location ID
- Contract Task Order number

- Sample ID
- Matrix
- Preservative
- Analysis to be performed
- Laboratory name

3.2 Select the container(s) that are appropriate for a given sample. Select the sample-specific ID label(s), complete date, time, and sampler name, and affix to the sample container(s).

3.3 Fill the appropriate containers with sample material. Securely close the container lids without overtightening.

3.4 Place the sample container in a sealable polyethylene bag and place in a cooler containing ice.

Example of a sample label is attached at the end of this SOP.

4.0 ATTACHMENTS

1. Sample Label

ATTACHMENT 1

SAMPLE LABEL

Tetra Tech NUS, Inc. 661 Andersen Drive Pittsburgh, 15220 (412)921-7090	**Project:** **Location:** **CTO:**	
Sample No:		**Matrix:**
Date:	**Time:**	**Preserve:**
Analysis:		
Sampled by:	**Laboratory**	

STANDARD OPERATING PROCEDURE

SOP-02

SAMPLE IDENTIFICATION NOMENCLATURE

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to establish a consistent sample nomenclature system that will facilitate subsequent data management at the Naval Air Station Corpus Christi Naval Auxiliary Landing Field Waldron. The sample nomenclature system has been devised such that the following objectives can be attained.

- Sorting of data by site, location, or matrix
- Maintenance of consistency (field, laboratory, and database sample numbers)
- Accommodation of all project-specific requirements
- Accommodation of laboratory sample number length constraints
- Ease of sample identification

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Writing utensil (preferably black pen with indelible ink)
Sample container labels

3.0 SAMPLE IDENTIFICATION NOMENCLATURE

3.1 <u>Samples</u>

All samples will be properly labeled with a sample label affixed to the sample container. Each sample will be assigned a unique sample tracking number.

3.1.1 Sample Numbering Scheme

The sample tracking number will consist of a four- or five-segment alpha-numeric code that identifies the sample's associated with the NALF Waldron site, sample type, location, and for aqueous samples, where applicable, whether a sample is filtered, and/or the sample round number. For soil samples, the final four

tracking numbers will identify the depth in units of feet below ground surface (bgs) at which the sample was collected. For sediment samples, the final four tracking numbers will identify the depth in units of inches bgs at which the sample was collected.

The alphanumeric coding to be used is explained in the following diagram and subsequent definitions:

AA	**AA**	**NN**	**NNNN (Soils and Sediment only)**
Site Acronym	Matrix	Sample Location Number	Sequential depth interval from freshly exposed surface

Character Type:

A = Alpha

N = Numeric

Site Name (NN):

SR = Skeet Range

Matrix Code (AA):

SS = Surface Soil Sample

SB = Subsurface Soil Sample

SD = Sediment Sample

Location Number (NNa):

Sequential number beginning with “01” for each matrix.

Depth Interval:

This code section will be used for soil and sediment samples only.

The depth code is used to note the depth bgs at which a soil or sediment sample is collected. The first two numbers of the four-number code specify the top interval and the third and fourth specify the bottom interval in feet (soil) or inches (sediment) bgs of the sample. The depths will be noted in whole numbers only; further detail, if needed, will be recorded on the sample log sheet, boring log, logbook, etc.

3.1.2 Examples of Sample Nomenclature

A surface soil sample collected from the Skeet Range, sampling location 003, to a depth of 1 foot bgs would be labeled as “SRSS030001”. A sediment sample collected from the Skeet Range, sampling location 010, to a depth of 6 inches bgs would be labeled as “SRSD0100006”.

3.2 Field Quality Assurance/Quality Control (QA/QC) Sample Nomenclature

Field QA/QC samples are described in this UFP SAP. They will be designated using a different coding system than the one used for regular field samples.

3.2.1 QC Sample Numbering

The QC code will consist of a three- to four-segment alpha-numeric code that identifies the sample QC type, the date the sample was collected, and the number of this type of QC sample collected on that date.

AA	NNNNNN	NN
QC Type	Date	Sequence Number (per day)

Character Type:

A = Alpha

N = Numeric

QC Types:

FD = Field Duplicate

RB = Rinsate Blank

SB = Source Blank

TB = Trip Blank

The sampling time recorded on the Chain-of-Custody Form, labels, and tags for field duplicate samples will be 0000 so that the samples are "blind" to the laboratory. Notes detailing the sample number, time, date, and type will be recorded on the sample log sheets and will document the location of the duplicate sample (sample log sheets are not provided to the laboratory).

3.2.2 Examples of Field QA/QC Sample Nomenclature

The first duplicate of the day at Skeet Range site for a surface soil sample collected on March 24, 2008 would be designated as FD03240801.

The third duplicate of the day taken at Skeet Range site of a surface soil sample collected on April 12, 2008 would be designated as FD04120803.

The first trip blank associated with samples collected on March 18, 2008 would be designated as TB03180801.

STANDARD OPERATING PROCEDURE
SOP-03

SAMPLE CUSTODY AND DOCUMENTATION OF FIELD ACTIVITIES

1.0 PURPOSE

This Standard Operating Procedure (SOP) establishes the procedures for sample custody and documentation of field sampling and field analyses activities.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

The following logbooks, forms, labels, and equipment are required.

Writing utensil (preferably black pen with indelible ink)
Site logbook
Field logbook
Sample label
Chain-of-Custody Form
Custody seals
Equipment calibration log
Soil and Sediment Sample Log Sheet

3.0 PROCEDURES

This section describes custody and documentation procedures. All entries made into the logbooks, custody documents, logs, and log sheets described in this SOP must be made in indelible ink (black is preferred). No erasures are permitted. If an incorrect entry is made, the entry will be crossed out with a single strike mark, initialed, and dated.

3.1 Site Logbook

The site logbook is a hard-bound, paginated, controlled-distribution record book in which all major on-site activities are documented. At a minimum, the following activities and events will be recorded (daily) in the site logbook:

- All field personnel present
- Arrival/departure of site visitors
- Arrival/departure of equipment
- Start or completion of sampling activities
- Daily on-site activities performed each day
- Sample pickup information
- Health and safety issues
- Weather conditions

The site logbook is initiated at the start of the first on-site activity (e.g., site visit or initial reconnaissance survey). Entries are to be made for every day that on-site activities take place.

The following information must be recorded on the cover of each site logbook:

- Project name
- Project number
- Book number
- Start date
- End date

Information recorded daily in the site logbook need not be duplicated in other field notebooks but must summarize the contents of these other notebooks and refer to specific page locations in these notebooks for detailed information (where applicable). At the completion of each day's entries, the site logbook must be signed and dated by the field operations leader (FOL).

3.2 Field Logbooks

The field logbook is a separate dedicated notebook used by field personnel to document his or her activities in the field. This notebook is hardbound and paginated.

3.3 Sample Labels

Adhesive sample container labels must be completed and applied to every sample container. Information on the label includes the project name, location, sample number, date, time, preservative, analysis, matrix, sampler's initials, and the name of the laboratory performing the analysis.

3.4 Chain-of-Custody Form

The Chain-of-Custody Form (COC) is a multi-part form that is initiated as samples are acquired and accompanies a sample (or group of samples) as it is transferred from person to person. Each COC is numbered. This form must accompany any samples collected for laboratory chemical analysis. A copy of a blank COC form is attached at the end of this SOP.

The FOL must include the name of the laboratory in the "Remarks" section to ensure that the samples are forwarded to the correct location. If more than one COC is necessary for any cooler, the FOL will indicate "Page __ of __" on each COC. The original (top) signed copy of the COC will be placed inside a sealable polyethylene bag and taped inside the lid of the shipping cooler. Once the samples are received at the laboratory, the sample custodian checks the contents of the cooler(s) against the enclosed COC(s). Any problems are noted on the enclosed COC Form (bottle breakage, discrepancies between the sample labels, COC form, etc.) and will be resolved through communication between the laboratory point-of-contact and the Task Order Manager (TOM). The COC form is signed and retained by the laboratory and becomes part of the sample's corresponding analytical data package.

3.5 Custody Seal

The custody seal is an adhesive-backed label, and it is part of the chain-of-custody process and is used to prevent tampering with samples after they have been collected in the field and sealed in coolers for transit to the laboratory. The custody seals are signed and dated by the samplers and affixed across the opening edges of each cooler (two seals per cooler) containing environmental samples. The laboratory sample custodian will examine the custody seal for evidence of tampering and will notify the Tetra Tech TOM if evidence of tampering is observed.

3.6 Equipment Calibration Log

The Equipment Calibration Log is used to document calibration of measuring equipment used in the field. The Equipment Calibration Log documents that the manufacturer's instructions were followed for calibration of the equipment, including frequency and type of standard or calibration device. An Equipment Calibration Log must be maintained for each electronic measuring device requiring calibration. Entries must be made for each day the equipment is used.

3.7 Sample Log Sheets

The Soil and Sediment Sample Log Sheets are used to document the sampling of soils and sediments (see SOPs-05 and -08).

4.0 ATTACHMENTS

1. Chain-of-Custody Record
2. Equipment Calibration Log
3. Soil and Sediment Sample Log

ATTACHMENT 1

CHAIN-OF-CUSTODY RECORD

CHAIN OF CUSTODY | NUMBER | PAGE ____ OF ____

PROJECT NO:	SITE NAME:	PROJECT MANAGER AND PHONE NUMBER	LABORATORY NAME AND CONTACT:
SAMPLERS (SIGNATURE)		FIELD OPERATIONS LEADER AND PHONE NUMBER	ADDRESS
		CARRIER/WAYBILL NUMBER	CITY, STATE

STANDARD TAT ☐
RUSH TAT ☐ ☐ 24 hr. ☐ 48 hr. ☐ 72 hr. ☐ 7 day ☐ 14 day

DATE YEAR	TIME	SAMPLE ID	MATRIX	GRAB (G) COMP (C)	No. OF CONTAINERS	CONTAINER TYPE PLASTIC (P) or GLASS (G) / PRESERVATIVE USED / TYPE OF ANALYSIS												COMMENTS

	DATE	TIME		DATE	TIME
1. RELINQUISHED BY	DATE	TIME	1. RECEIVED BY	DATE	TIME
2. RELINQUISHED BY	DATE	TIME	2. RECEIVED BY	DATE	TIME
3. RELINQUISHED BY	DATE	TIME	3. RECEIVED BY	DATE	TIME

COMMENTS

DISTRIBUTION: WHITE (ACCOMPANIES SAMPLE) YELLOW (FIELD COPY) PINK (FILE COPY)

FORM NO. TINUS-001 3/99

ATTACHMENT 2
EQUIPMENT CALIBRATION LOG

Tetra Tech NUS, Inc.

EQUIPMENT CALIBRATION LOG

PROJECT NAME : _____ INSTRUMENT NAME/MODEL: _____

SITE NAME: _____ MANUFACTURER: _____

PROJECT No.: _____ SERIAL NUMBER: _____

Date of Calibration	Instrument I.D. Number	Person Performing Calibration	Instrument Settings		Instrument Readings		Calibration Standard (Lot No.)	Remarks and Comments
			Pre-calibration	Post-calibration	Pre-calibration	Post-calibration		

ATTACHMENT 3

SOIL AND SEDIMENT SAMPLE LOG SHEET

SOIL & SEDIMENT SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____
Project No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Sample ID No.: _____
Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA:

Date:	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Time:			
Method:			
Monitor Reading (ppm):			

COMPOSITE SAMPLE DATA:

Date:	Time	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Method:				
Monitor Readings (Range in ppm):				

SAMPLE COLLECTION INFORMATION:

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

MAP:

Circle if Applicable:

MS/MSD	Duplicate ID No.:

Signature(s):

STANDARD OPERATING PROCEDURE
SOP-04

DECONTAMINATION OF FIELD SAMPLING EQUIPMENT

1.0 PURPOSE

This Standard Operating Procedure (SOP) establishes the procedures to be followed when decontaminating non-dedicated field sampling equipment during the field investigations.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Writing utensil (preferably black pen with indelible ink)
Non-latex rubber or plastic gloves
Cotton gloves
Field logbook
Potable water
Deionized water
LiquiNox detergent
Brushes, spray bottles, paper towels, etc.
Container to collect and transport decontamination fluids

3.0 DECONTAMINATION PROCEDURES

3.1 Don non-latex and/or cotton gloves and decontaminate sampling equipment (in accordance with the following steps) prior to field sampling and between samples.

3.2 Rinse the equipment with potable water. Rinsing may be conducted by spraying with water from a spray bottle or by dipping. Collect the potable water rinsate into a container.

3.3 Wash the equipment with a solution of LiquiNox detergent. Prepare the LiquiNox wash solution in accordance with the instructions on the LiquiNox container. Collect the LiquiNox wash solution into a container. Use brushes or sprays as appropriate for the equipment. If oily residue has accumulated on the sampling equipment, remove the residue with an isopropanol wash and repeat the Liquinox wash.

3.4 Rinse the equipment with potable water. Rinsing may be conducted by spraying with water from a spray bottle or by dipping. Collect the potable water rinsate into a container.

3.5 Rinse the equipment with deionized water. Rinsing may be conducted by spraying with water from a spray bottle or by dipping. Collect the deionized water rinsate into a container.

3.6 Remove excess water by air drying, shaking, or by wiping with paper towels as necessary.

3.7 Document decontamination by recording it in the field logbook.

3.8 Containerized decontamination solutions will be managed in accordance with the procedures described in SOP-09 and this UFP SAP.

STANDARD OPERATING PROCEDURE

SOP-05

SOIL CORING AND SAMPLING USING HAND AUGER TECHNIQUES

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes the procedures for collecting surface and subsurface soil cores from unconsolidated overburden materials using hand augering techniques.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Disposable medical-grade gloves (e.g., latex, nitrile)
Writing utensil (preferably black pen with indelible ink)
Indelible marker
Stainless Steel Auger Buckets
Stainless Steel Extension Rods
Cross Handle
Required decontamination materials
Bentonite pellets
Sealable polyethylene bags
Sample labels
Shipping containers (containing ice)
Disposable plastic trowels or stainless steel trowels
Stainless steel mixing bowls
Sample containers: Sample containers are certified clean by the laboratory supplying the containers.
Soil Sample Log Forms
Daily Activity Logs
Chain-of-Custody Form
Soil Boring Log

3.0 BOREHOLE ADVANCEMENT AND SOIL SAMPLING USING A HAND AUGER

Hand Augers may be employed to collect the soil cores. A hand augering system generally consists of a variety of all stainless steel bucket bits (i.e. cylinders 6-1/2" long and 2-3/4", 3-1/4", and 4" in diameter), a series of extension rods (available in 2', 3', 4' and 5' lengths), a cross handle.

3.1 The hand auger can be used in a wide variety of soil conditions. It can be used to sample soil, both from the surface, or to depths in excess of 12 feet. However, the presence or rock layers and the collapse of the borehole normally contribute to its limiting factors.

Attach a properly decontaminated bucket bit into a clean extension rod and further attach the cross handle to the extension rod.

3.2 Clear the area to be sampled of any surface debris (vegetation, twigs, rocks, letter, etc.).

3.3 Turn the hand auger sampler into the ground to a depth of 1 foot. The 0- to 1-foot depth soil interval is considered to be the surface soil. Subsurface soil samples will be collected at depths greater than 1 foot below ground surface.

3.4 After reaching the desired depth, slowly and carefully withdraw the apparatus from the borehole.

3.5 Utilizing a properly decontaminated stainless steel trowel or disposable trowel, remove the sample material from the bucket bit and place into a sealable polyethylene bag. Note in a field notebook or on a standardized data sheet any changes in the color, texture or odor of the soil.

3.6 Thoroughly homogenize the sample material and write sample ID, date, and time on the bag with an indelible marker.

3.7 Complete required information on the Soil Sample Log Sheet (copy attached at the end of this SOP). Update the Chain-of-Custody (COC) Form.

3.8 Excess soil core materials will be returned to the hole and tamped. If insufficient soil is available to fill the hole to the ground surface, then bentonite pellets mixed with the soil will be used to backfill the hole.

3.9 Decontaminate all soil sampling equipment in accordance with SOP-04 before collecting the next sample.

3.10 Soil samples will be transported to the field office where a portion of the sample will undergo XRF analysis for lead (See SOP-14).

3.11 For soil samples selected for fixed-base laboratory analysis, a portion of the sample will be used to fill the required sample containers as supplied by the laboratory. The sample labels will be completed and affixed to the sample container. The samples will then be packaged and shipped to the fixed-base laboratory in accordance with SOP-11.

4.0 ATTACHMENTS

1. Soil and Sediment Sample Log Sheet

ATTACHMENT 1

SOIL AND SEDIMENT SAMPLE LOG SHEET

SOIL & SEDIMENT SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____
Project No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Sample ID No.: _____
Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA:

Date:	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Time:			
Method:			
Monitor Reading (ppm):			

COMPOSITE SAMPLE DATA:

Date:	Time	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Method:				
Monitor Readings (Range in ppm):				

SAMPLE COLLECTION INFORMATION:

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

MAP:

Circle if Applicable:

MS/MSD	Duplicate ID No.:

Signature(s):

STANDARD OPERATING PROCEDURE
SOP-09

MANAGEMENT OF INVESTIGATION-DERIVED WASTE

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes how investigation-derived waste (IDW) will be collected, segregated, classified, and managed during the field investigations at the NALF Waldron facility. The following types of IDW will be generated during this investigation:

- Decontamination solutions
- Personal protective equipment and clothing (PPE)
- Miscellaneous trash and incidental items

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Health and safety equipment (with PPE)
Decontamination equipment
Field logbook
Writing utensil (preferably black pen with indelible ink)
Plastic sheeting and/or tarps
55-gallon drums with sealable lids
IDW labels for drums
Wastewater container tanks
Plastic garbage bags

3.0 PROCEDURES

Management of IDW includes the collection, segregation, temporary storage, classification, final disposal, and documentation of the waste-handling activities if necessary.

3.1 Liquid Wastes

Liquid wastes that will be generated during the site activities include decontamination solutions from sampling equipment. These wastes will be collected and transported to a central location at NALF Waldron.

3.2 Solid Wastes

Solid wastes that may be generated during the site activities include collection of lead shot from surface soil samples. This waste will be containerized and handed over to the NAS Corpus Christi Environmental Department Manager at the conclusion of field activities.

3.3 PPE and Incidental Trash

All PPE wastes and incidental trash materials (e.g., wrapping or packing materials from supply cartons, waste paper) will be decontaminated (if contaminated), double bagged, securely tied shut, and placed in a designated waste receptacle at NALF Waldron.

STANDARD OPERATING PROCEDURE
SOP-10

BOREHOLE AND SOIL SAMPLE LOGGING

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes the standard procedures and technical guidance on the logging of soil cores.

2.0 FIELD FORMS AND EQUIPMENT

Knife
Ruler (marked in tenths and hundredths of feet)
Boring Log: An example of this form is attached.
Photoionization detector (PID)
Writing utensil (preferably black pen with indelible ink)

3.0 RESPONSIBILITIES

A field geologist or engineer is responsible for supervising all boring activities and assuring that each borehole is properly and completely logged.

4.0 PROCEDURES FOR BOREHOLE AND SAMPLE LOGGING

To maintain a consistent classification of soil, it is imperative that the field geologist understands and accurately uses the field classification system described in this SOP. This identification is based on visual examination and manual tests.

4.1 USCS Classification

Soils are to be classified according to the Unified Soil Classification System (USCS). This method of classification is detailed in Figure 1 (attached to this SOP).

This method of classification identifies soil types on the basis of grain size and cohesiveness.

Fine-grained soils, or fines, are smaller than the No. 200 sieve and are of two types: silt (M) and clay (C). Some classification systems define size ranges for these soil particles, but for field classification purposes, they are identified by their respective behaviors. Organic material (O) is a common component of soil but has no distinguishable size range; it is recognized by its composition. The careful study of the USCS will aid in developing the competence and consistency necessary for the classification of soils.

Coarse-grained soils will be divided into categories: rock fragments, sand, or gravel. The terms "sand" and "gravel" not only refer to the size of the soil particles but also to their depositional history. To insure accuracy in description, the term "rock fragments" will be used to indicate angular granular materials resulting from the breakup of rock. The sharp edges that are typically observed indicate little or no transport from their source area; and therefore, the term provides additional information in reconstructing the depositional environment of the soils encountered. When the term "rock fragments" is used, it will be followed by a size designation such as "(1/4 inchΦ-1/2 inchΦ)" or "coarse-sand size" either immediately after the entry or in the remarks column. The USCS classification would not be affected by this variation in terms.

4.2 Color

Soil colors will be described utilizing a single color descriptor preceded, when necessary, by a modifier to denote variations in shade or color mixtures. A soil could therefore be referred to as "gray" or "light gray" or "blue-gray." Because color can be utilized in correlating units between sampling locations, it is important for color descriptions to be consistent from one boring to another.

Colors must be described while the sample is still moist. Soil samples will be broken or split vertically to describe colors. Samplers tend to smear the sample surface, creating color variations between the sample interior and exterior.

The term "mottled" will be used to indicate soils irregularly marked with spots of different colors. Mottling in soils usually indicates poor aeration and lack of good drainage.

4.3 Relative Density and Consistency

To classify the relative density and/or consistency of a soil, the geologist is to first identify the soil type. Granular soils contain predominantly sands and gravels. They are non-cohesive (particles do not adhere well when compressed). Finer-grained soils (silts and clays) are cohesive (particles will adhere together when compressed).

Granular soils are given the USCS classifications GW, GP, GM, SW, SP, SM, GC, or SC (see Figure 1).

The consistency of cohesive soils is determined by performing field tests and identifying the consistency as shown in the following table.

CONSISTENCY FOR COHESIVE SOILS

Consistency	Standard Penetration Resistance (Blows per Foot)	Unconfined Compressive Strength (Tons/Sq. Foot by pocket penetration)	Field Identification
Very soft	0 to 2	Less than 0.25	Easily penetrated several inches by fist.
Soft	2 to 4	0.25 to 0.50	Easily penetrated several inches by thumb.
Medium stiff	4 to 8	0.50 to 1.0	Can be penetrated several inches by thumb with moderate effort.
Stiff	8 to 15	1.0 to 2.0	Readily indented by thumb but penetrated only with great effort.
Very stiff	15 to 30	2.0 to 4.0	Readily indented by thumbnail.
Hard	Over 30	More than 4.0	Indented with difficulty by thumbnail.

Cohesive soils are given the USCS classifications ML, MH, CL, CH, OL, or OH (see Figure 1).

The consistency of cohesive soils is determined by hand by determining the resistance to penetration by the thumb. The thumb determination methods are conducted on a selected sample of the soil, preferably the lowest 0.5 foot of the sample. The sample will be broken in half and the thumb pushed into the end of the sample to determine the consistency. Do not determine consistency by attempting to penetrate a rock fragment. If the sample is decomposed rock, it is classified as a soft decomposed rock rather than a hard soil. One of the other methods will be used in conjunction with it. The designations used to describe the consistency of cohesive soils are shown in the above-listed table.

4.4 Weight Percentages

In nature, soils are consist of particles of varying size and shape and are combinations of the various grain types. The following terms are useful in the description of soil:

Terms of Identifying Proportion of the Component	Defining Range of Percentages by Weight
Trace	0 - 10 percent
Some	11 - 30 percent
Adjective form of the soil type (e.g., sandy)	31 - 50 percent

Examples:

- Silty fine sand: 50 to 69 percent fine sand, 31 to 50 percent silt.
- Medium to coarse sand, some silt: 70 to 80 percent medium to coarse sand, 11 to 30 percent silt.
- Fine sandy silt, trace clay: 50 to 68 percent silt, 31 to 49 percent fine sand, 1 to 10 percent clay.
- Clayey silt, some coarse sand: 70 to 89 percent clayey silt, 11 to 30 percent coarse sand.

4.5 Moisture

Moisture content is estimated in the field according to four categories: dry, moist, wet, and saturated. In dry soil, there appears to be little or no water. Saturated samples obviously have all the water they can hold. Moist and wet classifications are somewhat subjective and often are determined by the individual's judgment. A suggested parameter for this would be calling a soil wet if rolling it in the gloved hand or on a porous surface liberates water (i.e., dirties or muddies the surface). Whatever method is adopted for describing moisture, it is important that the method used by an individual remains consistent throughout an entire field activity.

4.6 Classification of Soil Grain Size for Chemical Analysis

To determine the gross grain size classification (e.g., clay, silt, and sand) from the USCS classification described above, the following table will be used.

Gross Soil Grain Size Classification	USCS Abbreviation	Description
Clay	CL	inorganic clays of low to medium plasticity, gravelly clays, sandy clays, silty clays, lean clays.
	CH	inorganic clays of high plasticity, fat clays.
	OH	organic clays of medium to high plasticity, organic silts.
Silt	ML	inorganic silts and very fine sands, rock four, silty or clayey fine sands with slight plasticity.
	OL	organic silts and organic silty clays of low plasticity
	MH	inorganic silts, micaceous or diatomaceous fine sand or silty soils.

Gross Soil Grain Size Classification	USCS Abbreviation	Description
Sand	SW	well graded sands, gravelly sands, little or no fines.
	SP	poorly graded sands, gravelly sands, little or no fines.
	SM	silty sands, sand-silt mixtures.
	SC	clayey sands, sand-clay mixtures.

4.7 Summary of Soil Classification

In summary, soils will be classified in a similar manner by each geologist/engineer at a project site. The hierarchy of classification is as follows:

- Density and/or consistency
- Color
- Plasticity (optional)
- Soil types
- Moisture content
- Other distinguishing features
- Grain size
- Depositional environment

5.0 ATTACHMENTS

1. Figure 1 - Unified Soil Classification System
2. Boring Log

ATTACHMENT 1

FIGURE 1 - UNIFIED SOIL CLASSIFICATION SYSTEM

Unified Soil Classification System

Coarse Grained Soils (more than half of soil > No. 200 sieve)	Gravels (More than half of coarse fraction > no. 4 sieve size)	GW	Well graded gravels or gravel-sand mixtures, little or no fines
		GP	Poorly graded gravels or gravel-sand mixtures, little or no fines
		GM	Sandy gravels, gravel-sand-silt mixtures
		GC	Clayey gravels, gravel-sand-silt mixtures
	Sands (More than half of coarse fraction < no. 4 sieve size)	SW	Well graded sands or gravelly sands, little or no fines
		SP	Poorly graded sands or gravelly sands, little or no fines
		SM	Silty sands, sand-silt mixtures
		SC	Inorganic silts and very fine sands, rock flour, silty or clayey fine sands or clayey silts with slight plasticity
Fine Grained Soils (more than half of soil < No. 200 sieve)	Silts and Clays LL = < 50	ML	Inorganic silts and very fine sands, rock flour, silty fine sands or clayey silts with slight plasticity
		CL	Inorganic clays of low to medium plasticity, gravelly clays, sandy clays, lean clays
		OL	Organic silts and organic silty clays of low plasticity
	Silts and Clays LL = > 50	MH	Inorganic silts, micaceous or diatomaceous fine sand or silty soils, elastic silts
		CH	Inorganic silts of high plasticity, fat clays
		OH	Organic clays of high plasticity, organic silty clays, organic silts
Highly Organic Soils		Pt	Peat and other highly organic soils

Grain Size Chart

Classification	Range of Grain Sizes	
	U.S. Standard Sieve Size	Grain Size In Millimeters
Boulders	Above 12"	Above 305
Cobbles	12" to 3"	305 to 76.2
Gravel	3" to No. 4	76.2 to 7.76
coarse	3" to 3/4"	76.2 to 4.76
fine	3/4"to No.4	19.1 to 4.76
Sand	No. 4 to No. 200	4.76 to 0.074
coarse	No.4 to No. 10	4.76 to 2.00
medium	No. 10 to No. 40	2.00 to 0.420
fine	No. 40 to No. 200	0.420 to 0.074
Silt and Clay	Below No. 200	Below 0.074

Relative Density (SPT)

SANDS AND GRAVELS	BLOWS/FOOT
VERY LOOSE	0 – 4
LOOSE	4 – 10
MEDIUM DENSE	10 – 30
DENSE	32 – 50
VERY DENSE	OVER 50

Consistency (SPT)

SILTS AND CLAYS	BLOWS/FOOT
VERY SOFT	0 – 2
SOFT	2 – 4
MEDIUM STIFF	4 – 8
STIFF	8 – 16
VERY STIFF	16 – 22
HARD	OVER 32

ATTACHMENT 2

BORING LOG

Tetra Tech NUS, Inc.

BORING LOG

Page ___ of ___

PROJECT NAME: _____ BORING No.: _____
PROJECT NUMBER: _____ DATE: _____
DRILLING COMPANY: _____ GEOLOGIST: _____
DRILLING RIG: _____ DRILLER: _____

Sample No. and Type or RQD	Depth (Ft.) or Run No.	Blows / 6" or RQD (%)	Sample Recovery / Sample Length	Lithology Change (Depth/Ft.) or Screened Interval	MATERIAL DESCRIPTION: Soil Density/ Consistency or Rock Hardness	Color	Material Classification	USCS *	Remarks	PID/FID Reading (ppm): Sample	Sampler BZ	Borehole**	Driller BZ**

* When rock coring, enter rock brokeness.
** Include monitor reading in 6 foot intervals @ borehole. Increase reading frequency if elevated reponse read.

Drilling Area Background (ppm): ____

Remarks: _____

Converted to Well: Yes _____ No _____ Well I.D. #: _____

STANDARD OPERATING PROCEDURE
SOP-11

SAMPLE PRESERVATION, PACKAGING, AND SHIPPING

1.0 PURPOSE

This Standard Operating Procedure (SOP) describes the procedures for sample preservation, packaging, and shipping to be used in handling soil, sediment, and aqueous samples.

2.0 REQUIRED FIELD FORMS AND EQUIPMENT

Shipping labels
Custody seals
Chain-of-custody (COC) form(s)
Sample containers with preservatives: All sample containers for analysis by fixed-base laboratories will be supplied, with preservatives added (if required) and deemed certified clean by the laboratory.
Sample shipping containers (coolers): All sample shipping containers are supplied by the laboratory.
Packaging material: Bubble wrap, sealable polyethylene bags, strapping tape, etc.

3.0 PROCEDURES FOR SAMPLE PRESERVATION, PACKAGING, AND SHIPPING

3.1 The laboratory provides sample containers with preservative already included (as required) for the analytical parameter for which the sample is to be analyzed. All samples will be held, stored, and shipped at 4°C. This will be accomplished through refrigeration (used to hold samples prior to shipment) and/or ice.

3.2 The sampler shall maintain custody of the samples until the samples are relinquished to another custodian or to the common carrier.

3.3 Check that each sample container is properly labeled, the container lid is securely fastened, and the container is sealed in a polyethylene bag.

3.4 If the container is glass, place the sample container into a bubble-out shipping bag and seal the bag using the self-sealing, pressure sensitive tape supplied with the bag.

3.5 Inspect the insulated shipping cooler. Check for any cracks, holes, broken handles, etc. If the cooler has a drain plug, make certain it is sealed shut, both inside and outside of the cooler. If the cooler is questionable for shipping, the cooler must be discarded.

3.6 Put ice into sealable polyethylene bags and place a layer of the sealed bags on the bottom of the cooler. Place the sample containers into the shipping cooler on top of the ice in an upright position (containers will be upright, with the exception of any 40-ml vials). Place sealable polyethylene bags of ice flat against the sides of the cooler. Continue filling the cooler with samples until the cooler is nearly full and the movement of the sample containers is limited.

3.7 Add a final layer of ice sealed in polyethylene bags to the top of the samples just before the cooler is closed and sealed.

3.8 Place the original (top) signed copy of the COC form inside a sealable polyethylene bag. Tape the bag to the inside of the lid of the shipping cooler.

3.9 Close the cooler and seal the cooler with approximately four wraps of strapping tape at each end of the cooler. Prior to wrapping the last wrap of strapping tape, apply a signed and dated custody seal to each side of the cooler (one per side). Cover the custody seal with the last wrap of tape. This will provide a tamper evident custody seal system for the sample shipment.

3.10 Affix shipping labels to each of the coolers, ensuring all of the shipping information is filled in properly. Overnight (e.g., FedEx Priority Overnight) courier services will be used for all sample shipments.

3.11 All samples will be shipped to the laboratory no more than 72 hours after collection. Under no circumstances should sample hold times be exceeded.

STANDARD OPERATING PROCEDURE

SOP-014

FIELD PORTABLE X-RAY FLUORESCENCE ANALYSIS OF SOIL AND SEDIMENT SAMPLES USING THE INNOV-X ALPHA SERIES INSTRUMENT

1.0 PURPOSE

This procedure is for the semiquantitative analysis of metallic lead particles and chemical compounds of lead in soil using a field portable x-ray fluorescence (FPXRF) spectrometer. This procedure is based on the United States Environmental Protection Agency (USEPA)-approved XRF field screening method for elemental analysis (Method 6200).

2.0 SCOPE, APPLICATION, AND LIMITATIONS

2.1 Scope of Procedure

Analysis of any other elements beside lead using FPXRF may require changes to this Standard Operating Procedure (SOP), and are therefore outside the scope of this SOP.

Although it is possible to use FPXRF to measure analytes in situ, this SOP requires removal of a soil sample from its native environment prior to analysis. By removing and homogenizing the sample prior to analysis, more precise and accurate results are obtained.

2.2 Analyst Training

Use of this method is restricted to personnel both trained and knowledgeable in the operation of the Innov-X alpha series XRF instrument or under the supervision of a trained and knowledgeable individual. Proper training for the safe operation of the instrument should be completed by the analyst prior to analysis. This training may be obtained directly from INNOV-X, an INNOV-X instrument distributor or lessor, or another trained Tetra Tech person.

3.0 ACRONYMS AND ABBREVIATIONS

FPXRF: Field portable x-ray fluorescence.
mg/kg: milligrams per kilogram.
MDL: Method detection limit.
PQL: Practical quantitation limit.
QC: Quality control.
RPD: Relative percent difference.
USGS: United States Geological Survey.
XRF: X-ray fluorescence.

4.0 RESPONSIBILITIES

Analyst/Chemist - Responsible for all aspects of sample preparation and analysis including equipment maintenance. Also responsible for maintaining chain-of-custody of samples after receipt from sampling personnel.

5.0 PROCEDURES

5.1 Safety

5.1.1 Radiation Safety

Radiation safety practices for the INNOV-X instrument can be found in the operator's manual. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer.

An additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply. The danger of electric shock is as substantial as the danger from radiation but is often overlooked because of its familiarity.

5.1.2 Protective Equipment

Analysts must wear disposable plastic gloves whenever sample aliquots are being transferred from one vessel to another. Consult the health and safety plan for other protection requirements.

5.2 Apparatus and Materials

Apparatus and materials consist of the following:

INNOV-X Alpha Series FPXRF spectrometer with data processing unit (iPAQ) pocket personnel computer):

INNOV-X Alpha Series XRF instrument manual to match the INNOV-X Alpha Series instrument.

Calibration verification check sample: A National Institute of Standards and Technology (NIST) or other Standard reference material (SRM) that contains lead in a concentration range that is compatible with the project objectives to verify the accuracy of the instrument. SRMs can be obtained from the NIST, the U.S. Geological Survey (USGS), the Canadian National Research Council, and the national bureau of standards in foreign nations. Pertinent NIST SRMs for FPXRF analysis include 2704, Buffalo River Sediment; 2709, San Joaquin Soil; and 2710 and 2711, Montana Soil. These SRMs contain soil or sediment from actual sites that has been analyzed using independent inorganic analytical methods by many different laboratories. Acceptable limits for SRM percent recoveries are usually provided with the SRM. In their absence, a limit of ± 30 percent will be used as a guideline.

Instrument Blank: May be silicon dioxide, a Teflon block, a quartz block, "clean" sand, or lithium carbonate.

Lead calibration check standard: Supplied by the FPXRF manufacturer.

Method blank material for performing method blank checks: May be lead-free silica sand or lithium carbonate that undergoes the same preparation procedure as the samples.

Battery charger.

Polyethylene sample cups: 31 millimeters (mm) to 40 mm in diameter with collar, or equivalent (appropriate for FPXRF instrument).

X-ray window film: Mylar™, Kapton™, Spectrolene™, polypropylene, or equivalent; 2.5 to 6.0 micrometers (µm) thick.

Sample containers: glass or plastic to store samples.

Sieves: 10-mesh Stainless steel, Nylon, or equivalent for preparing soil and sediment samples if necessary.

Trowels: for collecting soil samples.

Plastic bags: used for collection and homogenization of soil samples. May also be used as sample presentation device.

Rolling pin (optional): Wooden rolling pin for crushing samples.

5.3 Sample Collection, Preservation, and Handling

Samples shall be provided to the FPXRF analyst in plastic bags. The analyst is responsible for maintaining chain-of-custody of all samples until all analyses have been successfully completed. No sample preservation is necessary. All samples shall be handled in accordance with sample handling SOPs in effect for the field event.

5.4 Preventive Maintenance

Refer to the instrument manual for specific manufacturer's recommendations.

5.5 Instrument Start-Up

5.5.1 Ensure the pocket PC (iPAQ) is plugged into the FPXRF instrument body and install a fully charged battery into the instrument.

5.5.2 Press the ON/OFF button on the base of the pistol grip of the instrument. If the iPAQ does not automatically power up, press the Power button in the right corner of the iPAQ.

5.5.3 Tap the Microsoft icon at the upper left corner of the iPAQ.

5.5.4 Chose START.

5.5.5 Tap "Soil Mode" on the menu or choose Mode (bottom of screen) and then choose Soil Mode from the drop down menu.

5.5.6 Allow the instrument to warm up (approximately 3 minutes).

5.5.7 Release the manual trigger lock.

5.5.8 Standardize the instrument in accordance with Section 5.6.

5.6 Standardization/Calibration Check

It is not possible to start an analysis if the instrument has not been standardized. To verify proper calibration of the instrument it is necessary to periodically standardize it using the automated standardization procedure. This must be done anytime the instrument is restarted and every 4 hours of operation, although re-standardization may be done at any other time (e.g., when instrument drift is suspected).

5.6.1 Click the standardization piece (supplied with the instrument) on the front of the instrument, verifying that the solid portion of the standard completely covers the analysis window.

5.6.2 Select "Tap here to Standardize" or select *File → Standardize*. The red light on top of the instrument will blink indicating that the instrument is producing x-rays and the shutter is open. The amber light on the rear of the instrument will also be illuminated and a status bar will appear to display the progress of the standardization.

5.6.3 Upon successful standardization the message "Successful Standardization" will appear along with the instrument resolution. In this case tap "ok" to dismiss the completion message. If problems are encountered, either follow the prompts that appear and/or repeat the standardization. Contact the FOL if problems persist. Take note of any error messages that appear as they may be useful if the instrument manufacturer must be contacted. Additional assistance is also available in the manufacturer's instrument manual.

5.7 Quality Control

The quality control (QC) program includes analysis of blanks calibration verification checks, duplicate analyses, and field duplicate samples. For all the above areas, any identified problems and corrective action must be documented in the instrument run log, analysis narrative report, and instrument maintenance log or standards log (as applicable). Identical operating conditions will be used for each sample.

5.7.1 Laboratory Blanks

Two types of blank samples shall be analyzed for FPXRF analysis: instrument blanks and method blanks.

5.7.1.1 At the beginning of each day, at the end of each day, and after every 20th sample or when potential contamination of the instrument is suspected, analyze an instrument blank to verify that no contamination exists in the spectrometer or on the probe window.

If the lead concentration in the blank exceeds the method detection limit (MDL), see Section 5.9.3) check the probe window and other potentially contaminated instrument components for contamination. If contamination is not causing the elevated blank readings, “zero” the instrument according to manufacturer's instructions.

5.7.1.2 After every 20th sample analyze a method blank. If the method blank lead concentration exceeds the practical quantitation limit (PQL, see Section 5.9.4), identify the cause of the elevated lead concentration and reanalyze all samples since the last acceptable method blank.

5.7.2 Calibration Verification Checks

5.7.2.1 After performing each blank check (Section 5.7.2), analyze a calibration verification check sample to check the accuracy of the instrument and to assess the stability and consistency of the analysis for the analytes of interest.

5.7.2.2 If the measured lead percent recovery (See Section 5.9.1) is less than 60 percent or greater than 135 percent, reanalyze the check sample. If the value continues to fall outside this acceptance range, the instrument should be recalibrated, or restandardized according to the manufacture instructions and the batch of samples analyzed before the unacceptable calibration verification check must be reanalyzed.

5.7.3 XRF Duplicate Samples

XRF duplicate samples are two portions of the same sample that have been prepared and homogenized together, and then split and analyzed in the same manner by the XRF analyst.

5.7.3.1 Analyze an XRF duplicate at a frequency of 1 per 20 or once per day, whichever is more frequent.

5.7.3.2 If the computed RPD (See Section 5.9.2) exceeds 50 percent reanalyze both samples. If the RPD again exceeds 50 percent RPD consider whether the high degree of imprecision is caused

by sample heterogeneity or other causes. This assessment may be aided by repeating the analysis of a sample that was analyzed previously. If the observed imprecision is attributed to sample heterogeneity, increase the number of readings made per sample to try to limit the imprecision and repeat the analyses. If this does not correct the problem notify the FOL.

5.8 Sample Analysis

Note:

This section provides sample analysis instructions, assuming that appropriate instrument start-up and calibration checks have been completed. The longer the instrument count time, the lower the detection limits and the less uncertainty there is with a recorded result. Count time is user-selectable through the instrument's software. Because the XRF data will be used in a screening capacity to make preliminary decisions concerning the soil concentrations relative to 400 mg/kg, it is not necessary to obtain a high degree of accuracy or precision with the instrument. Therefore, count times should be limited to less than 180 seconds unless a usually high degree of precision is expected. To change the count time, select Options → Setup Testing and enter the same value (in seconds) to minimum and maximum count times.

Note:

Section 5.7 identifies the appropriate frequencies for conducting various QC sample analyses and the associated acceptance limits and corrective actions for potentially unsuitable conditions. The specified QC analysis frequencies are minimum frequencies. More frequent QC sample analyses are permitted, especially when diagnosing quality problems.

5.8.1 Ensure that calibration checks and blanks have been analyzed according to Sections 5.6, 5.7.1, and 5.7.2. Count times shall be at least 60 seconds but generally less than 180 seconds.

5.8.2 Acquire enough soil sample to fill an 8-ounce jar and separate from it all particles greater than the size of a pea.

5.8.3 Homogenize the remaining finer grained portion of the sample by simple mixing until it appears as uniform in texture and composition as practicable. Mixing may be done in a beaker or other suitable lead-free container. If the sample is moist and has high clay content, it may be kneaded in a plastic bag. Mixing shall continue for at least two minutes to ensure that the sample is well mixed. To aid mixing, the sample may be placed into a thick-walled (3 mil or thicker) gallon-sized freezer bag (e.g., ZipLoc®) and rolled flat with a rolling pin to break up large chunks of dirt.

5.8.4 Place a portion (approximately 1.5 cubic inches) of the homogenized sample aliquot into the instrument manufacturer's recommended sample cup (e.g., a 31.0-mm polyethylene sample cup (or equivalent) or place it in a thin-walled (1.0 mil or thinner) plastic sandwich bag (e.g., ZipLoc®).

5.8.5 If using a disposable plastic sample cup, ensure the cup is at least three-quarters full and cover with mylar (or other) film per the manufacturer's recommendations.

5.8.6 Present the sample to the instrument in Soil Mode.

5.8.7 Perform a single pull of the trigger to start the count. The count time shall be the same as was used for the calibrations, calibration checks, and blank analyses. The message "Test in progress" will appear on the instrument and the red light on top of the instrument and will illuminate.

5.8.8 When the predetermined count period has expired the message "Test complete" will appear on the instrument. A slight delay may also be incurred during which time the message "calculating" may appear to indicate that results are being computed.

5.8.9 Record the displayed results for lead concentration in mg/kg and the associated error on Figure 1.

CAUTION

Inconsistent positioning of samples in front of the probe window is a potential source of error because the x-ray signal decreases by the square of the distance from the radioactive source. This error is minimized by maintaining the same distance between the window and each sample. For the best results, the window of the probe should be in direct contact with the sample, which means that the sample surface should be flat and smooth to provide a good contact surface.

5.8.10 Remix the sample in the plastic bag (or rotate the sample cup approximately one-third of a turn) then acquire another measurement by repeating Steps 5.8.7 and 5.8.8. Record the result and associated error on Figure 1.

5.8.11 Repeat Step 5.8.10. Record the result and associated error on Figure 1 (XRF Field Form).

5.8.12 Based on the degree of precision demonstrated by the three individual measurements, determine whether additional readings should be acquired on the sample. This determination shall be based on professional judgment of the FPXRF analyst and shall consider the degree of precision observed during calibration checks and previous sample analyses. The objective will be to ensure that the average reading reported for each sample is representative of the true sample concentration. If the analyst feels that non-representative readings are being obtained the analyst shall correct the analytical system or notify the FOL prior to continuing with analyses.

5.8.13 Ensure that measured results are reported to the following standards

- Results < 1000 mg/kg (or parts per million) are reported to two significant figures and results > 1000 mg/Kg are reported to three significant figures.
- All values < MDL shall be reported as the MDL and flagged with the letter "U".
- All values > MDL and < PQL shall be reported as is and flagged with the letter "B".

5.9 Calculations

5.9.1 Percent Recovery: The equation for determining percent recovery of calibration verification check standards and standard reference materials is:

$$\%R = \frac{\text{Experimental Concentration}}{\text{Certified or Known Concentration}} \text{ X } 100\,\%$$

5.9.2 Relative Percent Difference: The equation for determining relative percent difference for laboratory and field duplicate samples is:

$$\text{RPD} = \frac{|\text{Amount in Sample 1} - \text{Amount in Sample 2}|}{0.5\,(\text{Amount in Sample 1} + \text{Amount in Sample 2})} \text{ X } 100\,\%$$

5.9.3 Method Detection Limit (MDL): Because the analyses governed by this SOP are semi-quantitative, the manufacturer-specified detection limit will be reported as the MDL unless the specified detection limit is less than 20 mg/kg. Care will taken to ensure that the appropriate count time is consistent with the reported detection limit. However, no value less than 20 mg/kg will be reported as an MDL.

5.9.4 Practical Quantitation Limit (PQL): Multiply the MDL by 3 to obtain the PQL: PQL = MDL*3

6.0 REFERENCES

Innov-X Systems, Inc. Innov-X Systems X-Ray Fluorescence Spectrometers Instruction Manual. Woburn, MA. June 2002.

Stephen Shefsky, NITON Corporation. Comparing Field Portable X-Ray Fluorescence (XRF) To Laboratory Analysis of Heavy Metals In Soil. Presented at the International Symposium of Field Screening Methods for Hazardous Wastes and Toxic Chemicals. Las Vegas, Nevada. January 29-31, 1997.

USEPA (U.S. Environmental Protection Agency), Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment, Office of Solid Waste, Washington, D.C. January 1998.

USEPA, Region I, Northeast Waste Management Officials' Association (NEWMOA) Technology Review Committee Advisory Opinion. Innovative Technology: X-Ray Fluorescence Field Analysis. September 21, 1999.

FIGURE 1

FIELD PORTABLE XRF SAMPLE ANALYSIS LOG SHEET

Page___ of ___

Project Site Name:	________________	Run Length/Duration:	________________
Project No.:	________________	Measurement Units:	________________
Analyzed By:	________________	Reference/Calibration:	________________

SAMPLING AND FIELD PORTABLE XRF RESULTS DATA:

SAMPLE ID	ANALYSIS DATE	ANALYSIS TIME	ELEMENT ANALYSIS	RESULT RUN 1	RESULT RUN 2	RESULT RUN 3	RESULTS AVERAGE	ERROR RUN 1	ERROR RUN 2	ERROR RUN 3	ERROR AVERAGE

APPENDIX C

LABORATORY STANDARD OPERATING PROCEDURES

METALS DIGESTION/PREPARATION

METHODS

USEPA SW846

3005A, 3010A, 3030C, 3031, 3050B

USEPA CLPILM 04.1 Aqueous & Soil/Sediment (NJDEP does not accept CLPILM 04.1 after June, 2003)

Addendum for USEPA CLPILM 05.2 Aqueous & Soil/Sediment

USEPA Methods for Chemical Analysis of Water and Wastes

200.7, Standard Methods 3030C

SOP NUMBER: **SOP-100**

REVISION NUMBER: **19**

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

07/25/06

EFFECTIVE DATE

04/10/08

DATE OF LAST REVIEW

METALS DIGESTION/PREPARATION

References:
Methods 3005A/USEPA CLPILM0 4.1 Aqueous, 3010A, 3030C, 3031, 3050B
USEPA CLPILM0 4.1 (Soil/Sediment), 200.7, Standard Methods 3030C
See Addendum for USEPA CLPILM 05.2 (Aqueous & Soil/Sediment)

I. SCOPE AND APPLICATION

A. AQUEOUS

1. Method 3005A and USEPA CLP ILM0 4.1, "Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by ICP Spectroscopy".

   a. This method is used to prepare surface water, ground water, drinking water and wastewater samples for analysis by inductively coupled argon plasma spectroscopy (ICP).

2. Method 200.7, "Determination of Metals and Trace Metals in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry"

   a. This method is used to prepare surface water, ground water, drinking water and wastewater samples for analysis by inductively coupled argon plasma spectroscopy (ICP).

3. Method 3010A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy".

   a. This method is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis by ICP. The procedure is used to determine total metals.

4. Method 3030C (Standard methods), "Preliminary Treatment for Acid-Extractable Metals".

   a. This method is used to prepare ground water samples from North Carolina for analysis by ICP.

B. SOLIDS

1. Method 3050B, "Acid Digestion of Sediments, Sludges and Soils".

   a. This method is used to prepare sediments, sludges and soil samples for analysis by ICP. Since certain matrices may result in poor recovery, the method of standard additions may be used when analyzed.

   b. It should be noted that some metals could be biased high with the soil digestion when dilution is necessary. Take necessary measures to ensure that dilutions are made as accurately as possible.

2. USEPA CLP ILM0 4.1, “Acid Digestion of Soil/Sediment”

   a. This method is used to prepare sediments and soil samples for analysis by ICP. Since certain matrices may result in poor recovery, the method of standard additions may be used when analyzed.

C. OILS

1. Method 3031, "Digestion Procedure for Oils".

   a. This method is used to prepare samples containing oils, greases or waxes for analysis by inductively coupled argon plasma emission spectroscopy (ICP).

D. **NOTES:**

1. "Total Metals" includes all metals, inorganically and organically bound and both dissolved and particulate.

2. "Dissolved metals" includes all metals present in a sample after filtration through a 0.45 micron filter followed by digestion.

II. SUMMARY OF METHODS

A. A representative sample of water, soil or oil is put into an acid medium and exposed to heat for a certain amount of time. This allows for reduction of interferences by organic matter and converts metals bound to particulates to form the free metal that can be determined by ICP-Atomic Emission Spectrometry.

NOTE: When a reporting limit is required for a project lower then is customary, a four times concentration must be used in order to reach that lower level. Care

must be taken to matrix match this concentrated aliquot. A blank and laboratory control sample (at a reduced concentration) are required with this concentration. A matrix spike (not at reduced concentration) and duplicate or matrix spike and matrix spike duplicate is needed per 20 samples or per batch.

III. SAMPLE HANDLING AND PRESERVATION

A. AQUEOUS

1. Samples are taken in high density polyethylene, one liter bottles. Samples should be preserved with concentrated HNO_3 to a pH <2 immediately once sampled. If dissolved metals are to be analyzed the sample should be filtered before the HNO_3 is added. The samples should be maintained at 4°C until analysis. The holding time for metals samples is 180 days or approximately 6 months.

B. SOLIDS

1. Samples are taken in high density polyethylene(CLP only) or glass bottles. The samples should be maintained at 4°C until analysis. The holding time for metals samples is 180 days or approximately 6 months.

C. OILS

1. Samples are taken in high density polyethylene bottles. The samples should be maintained at 4°C until analysis. The holding time for metals samples is 180 days or approximately 6 months.

IV. INTERFERENCES

A. AQUEOUS

1. Method 3005A and USEPA CLPILM0 4.1, "Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by ICP Spectroscopy", SW846, July, 1992.

   a. This digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

2. Method 200.7

3. Method 3010A

   a. See method 6010B.

B. SOLIDS

1. Method 3050B

   a. Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether this method is applicable to a given waste.

2. USEPA CLP ILM0 4.1

   a. Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether this method is applicable to a given waste.

C. OILS

1. Method 3031

   a. These digestates can have very high dissolved solids, which may necessitate the use of internal standards, dilutions, or the method of standard addition.

V. SAFETY

A. Normal accepted laboratory safety practices should be followed while performing this analysis.

B. Be certain the exhaust hood is functioning before you begin the digestion procedure.

C. Hot acids can be extremely corrosive. Avoid inhalation or contact with skin.

VI. EQUIPMENT/APPARATUS

A. Fume hood, Labconco or equivalent.

B. Hot plate, Thermolyne cimarec-3 or equivalent source for use at 95°C. The temperature of the hot plate must be monitored via the use of a temperature blank.

C. Thermometer capable of reading 80 to 120 degrees C – ERTCO cat# 611-3-SC or equivalent.

D. Vacuum pump for filtering dissolved metals- Gast or equivalent.

E. Analytical balance capable of weighing to 0.01 gram. Mettler model BB300 or equivalent.

F. Beckman CS-6R centrifuge.

G. Various class A volumetric glassware and ribbed watchglasses, Pyrex or equivalent.

H. Whatman No. 41 filter paper or equivalent.

I. Whatman No. 42 filter paper or equivalent.

J. Whatman 0.45 micron filter paper or equivalent.

K. 250 mL beaker or other appropriate vessel such as polypropylene block digester tubes, watch glasses and caps.

L. Stirring device, e.g. magnetic stirrer, glass rod or equivalent.

M. Manual Sample Mill

N. Wiley Sample Mill

O. Clippers for cutting vegetation

NOTE: All glassware should be acid washed.

VII. REAGENTS AND STANDARD PREPARATION

A. REAGENTS

1. Metals grade Nitric acid (HNO_3). Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

2. Metals grade Hydrochloric acid (HCl). Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

3. 30% hydrogen peroxide reagent, ACS Grade. Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

4. Metals grade Sulfuric acid (H_2SO_4). Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

5. Reagent water (Deionized water).

6. Potassium Permanganate - Ultra pure grade. Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

7. Ammonium hydroxide, concentrated, reagent grade. Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

8. Ammonium phosphate, reagent grade- Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

9. Base oil, analyte-free. Oil should be analyzed to determine level of impurities. If method blank is < MDL, then the reagent can be used.

B. STANDARDS

1. Traceability

a. A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

b. All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date and the logbook where information is recorded. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

c. The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

2. PREPARATION

A. Laboratory control sample

1. Aqueous

a. This solution is prepared as follows: 50 mL concentrated HCl, 20 mL concentrated HNO_3, 1 mL of CLP-CAL-1, Solution A, 1 mL of CLP-CAL-1 Solution B, 0.25 mL of CLP-CAL-2, and 0.25 mL of CLP-CAL-3 diluted to 1 L in a volumetric flask. Use 50 mL (100 mL for strict CLPIlM0 4.1) for digestion. This solution is given a unique identifier and recorded in sample digestion logbook.

b. For four times concentrated samples: The solution is prepared as follows: 50 mL concentrated HCl, 20 mL concentrated HNO_3, 1mL CLPP-SPK-4 (Inorganic Ventures) (This solution contains 10 mg/L Selenium, 100 mg/L Antimony, 50 mg/L Cadmium and Thallium, 40 mg/L Arsenic and 20 mg/L Lead) to 1 L in a volumetric flask. This solution is given a unique identifier. Use 12.5 mLs to 50 mLs and prepare two aliquots. Heat at 90 to 95°C to reduce the volume in each vessel to ten mLs and then combine each 10 mL aliquot into one vessel and take to a final volume of 25 mLs. Take care to matrix match acids so that the final 25 mL portion will contain 2% HNO_3 and 5% HCl. Use 0.125 mLs HNO_3 and 0.3125 mLs HCl to each 50 mL vessel.

2. Solids

a. A 1.0 ±0.02 gram aliquot of teflon chips is weighed and spiked using the same spiking solution used for matrix spikes. This sample is given a unique identifier according to the Lot# for the teflon chips used and when digested is given the descriptor. i.e. LCSS(date)A and then B etc. plus the unique identifier number assigned. Alternatively a solid matrix standard reference material is obtained from the manufacturer. This sample is given a unique identifier and recorded in the sample digestion logbook.

3. Oils

a. **An analyte free oil MUST be used or explosive reactions can occur.** An analyte free oil (wesson oil which has been analyzed previously to prove that it is < MDL.) is spiked using the same spiking solution used for matrix spikes. This sample is given a unique identifier. i.e. LCSO(date)A and then B etc.

B. Spiking solution

1. Sample is spiked using 0.1 mL of CLP-CAL-1, Solution A, 0.1 mL of CLP-CAL-1 Solution B, 0.025 mL of CLP-CAL-2 and 0.025 mL of CLP-CAL-3 for a final volume of 100 mL. If only 50 mL is used, decrease amount used appropriately. These solutions are given unique identifiers. Record the amount spiked and the unique identifier of the standard.

2. CLP sample is spiked using 0.1 mL CLPP-SPK-1 and 0.1 mL CLPP-SPK-4 for a final volume of 100 mL. If only 50 mL is used, decrease amount used appropriately. These solutions are given unique identifiers.

3. For samples that require four times concentration, the sample is spiked using 0.0125 mLs of CLPP-SPK-4 to each of two vessels with 50 mLs of sample in each. The volume of each of the vessels is lowered to less then 10 mLs and combined and the final volume of this concentrated sample is 25mLs.

VIII. CALIBRATION

A. The temperature of the samples must be maintained at 95°C and monitored via a temperature blank. 85° for oil samples. Record in digestion logbook.

IX. PROCEDURE

A. Glassware preparation for oil digestion or when the hot-block can not be used:

1. Wash glassware with hot soapy water and rinse thoroughly. (Beakers must be washed as soon as possible after being used, dirty beakers must not be allowed to sit overnight.)

2. Rinse glassware with reagent water that contains 5% HNO_3 and 5% HCl followed by a rinse with reagent water.

3. Prior to use, all glassware must be confirmed clean via a glassware check. Otherwise, repeat step "2" until the glassware check passes.

B. Aqueous sample filtration (for dissolved metals):

1. Thoroughly clean a flask and funnel with hot soapy water. Next, rinse the flask and funnel with 1:5 HNO_3 followed by a thorough D.I. water rinsing. This step is very important because the filters contain some metals (namely Zn) which could contaminate the samples.

2. Rinse a 0.45 micron filter with 1:5 HNO_3 thoroughly, followed by D.I. water.

3. Filter the unpreserved sample. If dissolved Hg analysis is requested for the sample, filter at least 200 mL.

4. Discard the first 50 to 100 mL.

5. A preparation blank must be taken through the filtration step and analyzed with the sample.

6. Preserve the sample with HNO_3 to pH<2.

7. Soluble samples that are clean and clear do not have to be digested. Use 100 mL sample, add 5 mL of concentrated HCl and 2 mL of concentrated HNO_3. **Samples must be digested unless approval for analysis without digestion is received from the project manager.**

C. Aqueous sample preparation

1. Method 3005A and USEPA CLP ILM0 4.1, "**Acid digestion procedure for total recoverable or dissolved metals for analysis by ICP ".**

a. Shake sample thoroughly and pour 50 mL of the well-mixed sample into a digestion vessel. For samples which require concentration pour 50 mLs of the well-mixed sample into two digestion vessels.

b. Add 0.50 mL (1 mL of (1+1) when strict CLP ILM0 4.1 is required) concentrated HNO_3 to the sample. For samples which require concentration, add 0.125 mL (0.25 mL of (1+1) when strict CLP ILM0 4.1 is required) concentrated HNO_3 to the sample.

c. Add 2.5 mL (5 mL of 1+1) when strict CLP ILM0 4.1 is required) concentrated HCl to the sample. For samples which require concentration, add 0.3125 mL (0.625 mL of (1+1) when strict CLP ILM0 4.1 is required) concentrated HCl to the sample.

d. Cover the sample with a ribbed watch glass or equivalent source.

e. Transfer the digestion vessel to a pre-heated hot plate or hot block at 90 to 95°C. A temperature blank will assure correct temperature. The temperature must be recorded in the digestion log book. Take the volume down to between 5 to 10 mL, (12 to 25 mLs when strict CLP ILM0 4.1 is required) **making certain that the sample does not boil**. **This is extremely important. Boiling may lead to vaporization of certain analytes.** Remove the sample from the hot plate and cool

f. When necessary, filter or centrifuge the sample to remove insoluble material that could clog the nebulizer. The filtering apparatus must be thoroughly cleaned with dilute nitric acid prior to filtration.

g. Bring sample to its predigestion volume (or when samples require concentration, to a volume four times lower then what was started with) with DI water in the digestion vessel. The final volume must be recorded in the digestion log book.

h. The sample is now ready for analysis.

i. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards plus identification #'s for standards used for spiking and the volume spiked into the sample.

2 Method 200.7, "**Acid digestion procedure for total recoverable metals**".

a. Shake sample thoroughly and pour 50 mL of the well-mixed sample into the digestion vessel. If sample contains undissolved solids >1% refer to Section 11.3 of Method 200.7 for subsequent procedures.

b. Add 1.0 mL concentrated HNO_3 to the sample.

c. Add 2.50 mL concentrated HCl to the sample.

d. Cover the sample with a ribbed watch glass or equivalent source.

e. Transfer the digestion vessel to a pre-heated hot plate or equivalent source at 85°C. Take the volume down to between 10 to 15 mL, **making certain that the sample does not boil**. **This is extremely important. Boiling may lead to vaporization of certain analytes.**

f. Leave sample on hot plate and gently reflux for 30 minutes. Remove from hot plate and cool.

g. Bring sample to its predigestion volume with DI water in the digestion vessel.

h. When necessary, filter or centrifuge the sample to remove insoluble material that could clog the nebulizer. The filtering apparatus must be thoroughly cleaned with dilute nitric acid prior to filtration.

i. The sample is now ready for analysis.

j. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards.

3. Method 3010A, "**Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy**".

a. Shake sample thoroughly and pour 50 mL of the well-mixed sample into the digestion vessel.

b. Add 1.5 mL concentrated HNO_3 to the sample.

c. Cover the sample with a ribbed watch glass.

d. Transfer the digestion vessel to a pre-heated hot plate or hot block at 90 to 95°C. A temperature blank must be used, with the temperature being recorded in the log book. Take the volume down to a low

volume (~5 mL), **making certain that the sample does not boil**. **This is extremely important. Boiling may lead to vaporization of certain analytes. Also make certain that no portion of the bottom of the digestion vessel is allowed to go dry. This may lead to low recoveries.** Remove the sample from the hot plate and cool.

e. Add another 1.5 mL portion of concentrated HNO_3 to the sample.

f. Cover the sample with a ribbed watch glass.

g. Transfer the vessel to the hotblock or equivalent source. Increase the temperature so a gentle reflux occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).

h. Uncover the vessel and evaporate to a low volume (~3 mL) **making certain that no portion of the bottom of the digestion vessel is allowed to go dry.** Remove and cool.

i. Add 2.5 ml of 1:1 HCl (10 mL/100 mL of final solution).

j. Cover the digestion vessel and reflux for an additional 15 minutes.

k. Bring sample to its predigestion volume in digestion vessel.

l. When necessary, filter or centrifuge the sample to remove insoluble material that could clog the nebulizer. The filtering apparatus must be thoroughly cleaned with dilute nitric acid prior to filtration.

Note: When preparing USACE project samples, if any sample in a digestion batch requires filtration, all samples (including QC samples) must be treated in the same manner.

m. The sample is now ready for analysis.

n. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards.

4 Method 3030C (Standard Methods), "**Preliminary treatment for Acid-Extractable Metals"**

a. Shake sample thoroughly and pour 50 mL of the well-mixed sample into a 50 mL digestion vessel.

b. Add 2.5 mL 1:1 HCl to the sample.

c. Heat 15 minutes in a hot bath.

d. Filter through a membrane filter.

e. Adjust filtrate volume to 50 mL with DI water.

f. Transfer to ICP analyst.

D. Solid sample preparation

It is extremely important that waste (when appropriate), soil and sediment samples be mixed thoroughly to ensure that the sample is as representative as possible of the sample media. The most common method of mixing is referred to as quartering. The quartering procedure should be performed as follows:

- *The material in the sample pan(inorganic-plastic/organic-aluminum) should be divided into quarters and each quarter should be mixed individually.*
- *Two quarters should then be mixed to form halves.*
- *The two halves should be mixed to form a homogenous matrix.*

This procedure should be repeated several times until the sample is adequately mixed.

NOTE: Samples that are clay type materials should be handled in a different manner. Due to these type sample matrices having an affinity to stick to most anything that touches it, another approach must be followed. Obtain a representative sub-sample aliquot from the center or middle section of the sample container.

Grinding of Vegetation Samples

Remove sample from shipping container and brush off dirt particles. Chop sample into about half inch pieces with clippers or other cutting tool. Place the sample in an aluminum pan and air-dry in an exhaust hood to the appropriate dryness for grinding. It should be dry enough where it won't stick to the inside of the mill. Grind the dried sample to fineness in either the manual sample mill

or the Wiley mill or both if needed. Place the ground sample in a container and label immediately.

1. USEPA CLP ILM0 4.1, **"Acid digestion of Soil/Sediment"**

   a. Mix the sample thoroughly to achieve homogenity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 1.5 g portion of sample and transfer to a digestion vessel.

   b. Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass or equivalent source. Heat the sample to 92 to 95°C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5.0 mL of concentrated HNO_3, replace with watch glass or equivalent source, as appropriate, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the heating vessel.

   c. After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3.0 mL of 30% hydrogen peroxide (H_2O_2). Return the heating vessel to the hot plate or equivalent heating source for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the heating vessel.

   d. Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2.)

   e. If the sample is being prepared for ICP analysis of Al, As, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, and Zn, add 5 mL of 1:1 HCl and 10 mL of Type II water, return the covered heating vessel to the hot plate or equivelent heating source, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 50 mL with Type II water. NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. Dilute the digestate to 144 mL with DI water, add 5 mLs concentrated HCl and 1 mL of concentrated HNO_3, mix well and place into the appropriate container. The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3. The sample is now ready for analysis.

f. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards and ID of matrix spikes and the amounts used for spiking.

2. Method 3050B, **"Acid digestion of Sediments, Sludges and Soils"**

a. Mix the sample thoroughly for 5 minutes using a plastic spatula or Teflon coated spatula in a glass or plastic weigh boat to achieve homogeneity.

b. Weigh approximately (to the nearest 0.01 g) a 1 to 1.5 g portion of the sample directly into a digestion vessel. For samples with low percent solids a larger sample size may be used as long as digestion is completed. Record the exact mass in the digestion log.

NOTE: To achieve the lowest reporting limit possible, use a 2.0 g portion of sample with an ending volume of 100 mLs.

c. Add 5 mL D.I. water and 5 mL concentrated HNO_3(1:1), mix the slurry and cover with a watch glass. Place the sample in a preheated hot block and reflux at 95°C for 10 to 15 minutes being certain that the sample does not boil. Record temperature in digestion log book

d. Allow the sample to cool. Add 5 mL concentrated HNO_3, replace the watch glass and heat/reflux again for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of concentrated HNO_3) over and over until <u>no</u> brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a watch glass or equivalent allow the solution to evaporate to approximately 5 mL without boiling at 95°C $\pm$ 5°C for approximately two hours. Maintain a covering of solution over the bottom of the vessel at all times. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker. If the volume does get low, add 2.5 mL of D.I. water to bring volume back up.

e. Take the sample off the hot block and allow it to cool. Next, add 2 mL of D.I. water and 3 mL of 30% Hydrogen Peroxide. (The sample will bubble upon the addition of H_2O_2 if it is still warm.) Cover the vessel with a watch glass and return the sample to the hot block or equivalent source and heat until the bubbling subsides. Care must be taken to

ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker. Add two more 3 mL portions of H_2O_2 to the sample in the same manner as before. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2.)

f. Cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate at 95°C ± 5°C without boiling for approximately two hours until the volume has been reduced to approximately 2.5 mL. Maintain covering of solution over the bottom of the vessel at all times.

g. Add 2.5 mL of DI water and 2.5 mL of concentrated HCl and 10 mL of DI water, cover the sample with a ribbed watch glass and continue refluxing for an additional 10 minutes without boiling

h. When necessary, filter or centrifuge the sample to remove insoluble material that could clog the nebulizer. The filtering apparatus must be thoroughly cleaned with dilute nitric acid prior to filtration.

i. Bring sample up to 50 mL with D.I. water in the vessel. Add 150 ml of DI water to a 250 ml sample bottle. Invert the 50 ml sample digestion vessel several times to mix the sample and pour sample into the 150 ml of the sample bottle. Pour some sample back into the 50 ml sample digestion vessel to rinse and pour back into the 250 ml sample bottle and cap and mix.

NOTE1: When preparing USACE project samples, if any sample in a digestion batch requires filtration , all samples (including QC samples) must be treated in the same manner.

NOTE2: To achieve the lowest reporting limit possible use 2.0 grams of sample with an ending volume of 100 mLs.

j. The sample is now ready for analysis.

k. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards.

E. Oils

1. Method 3031, "**Digestion Procedure for Oils**"

NOTE: THIS METHOD IS VERY TIME CONSUMING--DISCUSS SUB-CONTRACTING SAMPLES WITH YOUR SUPERVISOR AS SOON AS THEY COME IN THE DOOR.

a. Homogenize sample and Weigh approximately (to the nearest 0.01 g) a 0.5 g representative portion of the sample into a 250 mL beaker. Separate and weigh proportional aliquots of the phases if more than one phase is present. Record the exact mass in the digestion log. Larger or smaller sample sizes can be used if needed.

g. Add 0.5 g of potassium permanganate powder. If larger sample sizes are used, increase the amount of potassium permanganate so that the ratio of oil to postassium permanganate is still 1:1. Mix the oil and permanganate thoroughly until homogenous. Thick oils and tars that cannot be mixed should be heated to achieve mixing (the oil may react mildly). It is important to record the amount of potassium permanganate used for each sample if analysis is by ICP-AES and correction is to be made for the amount of manganese. If more than 10% of the sample is aromatic material, such as xylene, then the reaction will be incomplete. If this is the case, increase the amount of potassium permanganate. If the sample is a mixture of oil and other non-organic materials, reduce the amount of potassium permanganate.

NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. This should include face shields and latex gloves.

h. Cautiously add 1.0 mL concentrated H_2SO_4, and stir with an appropriate stirring device. If larger sample sizes are used, increase the volume of the sulfuric acid so that the ratio of oil to sulfuric acid is 1 g to 2 mL. The H_2SO_4 can be added dropwise or all at once, depending on analytical needs. (Generally, dropwise is preferred when low reporting limits are needed.)

NOTE: To prevent a strong exothermic reaction, H_2SO_4 should be added dropwise to all samples unfamiliar to the analyst and to all samples that are known to be highly reactive.

The reaction can take several seconds to begin, but when it occurs it will be very quick, vigorous, and exothermic. Generally larger sample sizes will react faster than smaller. Likewise, lower average molecular weight materials will react faster than heavier. Do not be mislead by an initial lack of reactivity. A grey-white vapor will be ejected from the beaker (SO_3) and splattering and bubbling can occur. The beaker will become very hot. This step is complete when no more gases are given off and the sample would be a thick black lumpy paste. Allow the beaker to cool as needed.

NOTE: Care must be taken when working with very light organic materials, such as diesel fuels, as they may flash. Generally, the lower the average molecular weight of the meterial correlates to a greater danger of flashing. The danger of flashing is reduced by adding the sulfuric acid dropwise.

NOTE: If more than 10% of the sample is aromatic material, such as xylene, only a little grey-white vapor will form. This will reduce accuracy and complicate nebulization. If there is a signigicant amount of non-hydrocarbon material, a sputtering recation will occur and black MnO_2 particulates will be given off. See section (b.) above under procedure.

i. Add 2 mL of concentrated HNO_3 and stir. This reaction will be slightly exothermic. If larger sample sizes are used, it is not always necessary to increase the volume of HNO_3 proportionately, depending on analytical needs. Some reddish-brown vapor (NO_2) may be given off. Allow the reaction to continue until complete, that is when the digestate no longer gives off fumes. Allow the beaker to cool as needed.

j. Add 10 mL of concentrated HCl and stir. If larger sample sizes are used, it is not always necessary to increase the volume of HCl proportionately, depending on analytical needs. This reaction will be slightly exothermic and gas formation and foaming will occur. Lighter oils will foam more than will heavier oils. If excess foaming occurs, add water to prevent sample loss. Allow the beaker to cool as needed.

k. Heat the beaker until there is no further gas evolution. (temperature should not exceed 150 °C to prevent volatilization). There may be additional foaming or other milder reactions which may result in overflow from the beaker. If excess foaming occurs, either remove the beaker from the heating source until foaming subsides or add sufficient

water to prevent overflow. The final digestate should be a clear yellow liquid with black or dark reddish-brown particulates.

l. Filter the digestate through Whatman 41 filter paper and collect filtrate in a volumetric flask or beaker.

m. Wash the digestion beaker and filter paper, while still in the funnel, with no more than 5 mL of hot HCl.

   NOTE: The purpose of this next step is to recover antimony, barium, and silver that may not have been completely solubilized. If the sample is not being prepared for these analytes, the next step may be skipped.

n. (Optional) After having washed the filter paper, remove the filter and residue from the funnel and place it back in the beaker. Add 5 mL of conc. HCl and place the beaker back on the heating source until the filter paper dissolves (temperature should not exceed 150 °C ±5 °C to prevent volatilization). Remove the beaker from the heating source and wash the cover and sides with reagent grade water and then filter the residue and collect the filtrate in the same flask or beaker as in sections f. and g. above. Allow the filtrate to cool and quantitatively transfer to a volumetric flask. Bring to volume.

o. (Optional) If the filtrate is collected in a beaker, the filtrate can be heated again to drive off excess HC1. This can reduce matrix effects in sample introduction (temperature should not exceed 150 °C ± 5 °C to prevent volatilization). When sufficient HCl has been removed, remove the beaker from the heating source, allow to cool, and then transfer the contents to a volumetric flask and bring to volume. However, if too much HCl is removed, barium, silver and antimony can be lost.

p. Analyze the flitrate by ICP-AES. Depending on the final volume selected, the total solids in the digestate may be high enough to cause nebulization problems. Problems due to high dissolved solids may be corrected by 1) following optional Section i., 2) using internal standards, 3) using flow injection analysis, or 4) using other matrix correction procedures.

   Manganese Removal Steps

   NOTE: The purpose of these next steps is to remove the manganese in the digest by precipitating it as manganese ammonium phosphate

under alkaline conditions. Elements that do not form insoluble phosphates, such as arsenic, are filtered out and can be analyzed at lower concentrations.

q. Take the digestate, or portion of digestate and reduce the volume to remove as much HCl as possible without going below 10 mL. Then add conc. NH_4OH until pH is 7 or greater. For most matrices, the digestate will change colors (often from yellow to brown) at pH 7. A mild exothermic reaction will occur immediately.

r. Add at least 2 g ammonium phosphate for each 1 g of potassium permanganate used in the digestion and stir. An excess of phosphate is needed for good analyte recovery. Then add enough water and mix to ensure maxium precipitation. A pink or yellow silky amorphous precipitate, manganese ammounium phosphate, will form. If too much NH_4OH is used some of the manganese ammonium phosphate can be solubilized. Stir until precipitation is complete. Some ammonium phosphate may remain unreacted at the bottom of the beaker.

s. Filter the digestate through Whatman 41 filter paper (or equivalent) and collect filtrate in a volumetric flask or beaker.

t. Heat the filtrate to volatilize the ammonia (temperature should not exceed 150 °C ± 5 °C to prevent volatilization). The volume of filtrate can be reduced by heating to no less thatn 10 mL. If too much water is removed ay ammonium chloride formed will solidify. If this occurs, either add enough water to dissolve the solids or filter out the solids and wash the residue with deionized water. The filtrate can be analyzed by ICP-AES.

u. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards.

X. CALCULATIONS

A. The analyst must be supplied with both beginning sample masses/volumes and final digestate volumes. This information must be recorded in the digestion log.

XI. QUALITY CONTROL

A. Digestion

1. Temperature blank

   a. The temperature of the hot plate/hot block must be monitored for temperature during the digestion process.

   b. The thermometer must be tagged with annual calibration information. Record the thermometer reading, correction factor and the corrected temperature in the digestion log.

2. Blanks

   a. Digest a blank with every batch of samples digested (20 sample maximum). The blank is prepared by adding all the same reagents added to the samples to a clean dry beaker and taking it through the same process as the samples. **NOTE: The blank for OILs MUST include an analyte-free oil or explosive reactions can occur.**

   b. Also, there must be a blank for every different method of digestion that is set up that day, every 20 samples.

   c. There must also be a blank for every different matrix of samples that is to be digested, every 20 samples.

   d. Sample is given a unique identifier in the digestion log.

3. Laboratory Control Samples

   a. For water samples, one LCS is digested with every batch of samples digested (20 sample maximum).

   b. For water samples, a LCS is digested every day for each type of digestion, every 20 samples.

   c. For soil/sediment samples, a soil matrix standard reference material (SRM) must be digested per batch (20 samples maximum) or alternatively a spiked teflon chip sample.

   d. Sample is given a unique identifier in the digestion log.

   e. Recoveries of standard reference materials or laboratory control samples spiked with organo-metallic standards recoveries should be **±25% of their true values for OILS.**

4. Duplicates

   a. A duplicate is prepared every 20 samples. This usually takes the form of a matrix spike duplicate.

      NOTE: Certain projects require a sample duplicate and a matrix spike duplicate with each set of twenty samples.

5. Blank Spike

   a. This is required for certain projects.

B. Sample Matrix

NOTE: Field blanks/duplicates, trip blanks, or equipment blanks are not to be used for sample matrix QC samples.

1. Matrix spike

   a. Digest a spike and spike duplicate every 20 samples where sample volume is adequate to do so. Choose a sample (if possible) that has a lot of metals requested to be analyzed.

      NOTE: For some projects, a sample duplicate and sample spike may be required instead of a spike and spike duplicate. Your supervisor should make you aware of these projects.

   b. The following metals do not get digested spikes when using CLP spike.

      Calcium
      Magnesium
      Sodium
      Potassium

   v. For TCLP samples, a spike must be digested for every matrix. You should inspect the sample (original sample prior to extraction) or check the log book to determine matrix type. (Also the matrix spike aliquot must be added to the extract after filtration but before preservation.)

d. The CLH project requires that a high and a low spike be prepared and analyzed. Spikes shoud be prepared at 40 mg/Kg and 400 mg/Kg for soil samples and 200 ug/L and 2000 ug/L for aqueous samples.

XII. CORRECTIVE ACTIONS

A. Sample boils during digestion.

1. Redigest another sample aliquot.

B. Sample goes dry or portion of beaker bottom is exposed due to excess evaporation during digestion.

1. Redigest another sample aliquot.
2. Glass beaker dry for an extended period of time? Discard beaker.

XIII. SPECIAL NOTES

A. **Never** take for granted how a sample should be digested. If the sample looks strange or unusual, or if you are not sure what metals the sample gets, what detection limits are required, whether the sample is total or dissolved, or even what method of digestion should be used, always ask your supervisor or the person who is to analyze the sample. How metals need to be digested changes too often to take it for granted.

B. **Antimony (Sb) soils** should be analyzed within 48 hours of digestion whenever possible. When a soil requesting Antimony analysis is received, you must coordinate with the person who will be analyzing it to be sure that they can analyze it on the same day that it is digested.

C. Labels for the digested sample must be written in a neat and legible manner. The labels must include such information as sample number, client name, the date digested, and the volume or mass digested.

D. There are several precautions that must be taken to minimize the possibility of contamination.

1. All metals glassware must be kept separate from all other laboratory glassware.

2. Metals glassware must be washed as soon as possible after being used. **Dirty metals beakers must not be left overnight.**

3. Acid to be used for metals digestions must be kept separate from all other laboratory acid.

E. Samples must be digested in a timely manner to ensure ICP analysis remains on schedule for data generation. Samples received on or before Wednesday of week X must be prepared for ICP digestion by the end of week X. Your supervisor must be consulted if this schedule can not be met at a particular time.

F. Please consult Waste Disposal SOP-405, for information concerning disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

The following is a list of changes for sample preparation when the 5.2 statement of work is required:

1. Soluble samples are required to be digested unless the chain of custody specifically states that digestion is not required. An MDL study must be done on the unprepared MDL solution in order to provide MDL levels for samples that are not digested. When digestion is not required an LCSW and post digestion spike are not required.

2. Digestates must be stored until 365 days after delivery of a complete, reconciled data package.

3. Preparation codes are used on form 13's. They are found in the 5.2 statement of work page B-39 3.4.12.2.4.

DEFINITIONS – Refer to SOP-431 for common environmental laboratory definitions.

MERCURY ANALYSIS IN WATER

BY MANUAL COLD VAPOR TECHNIQUE

METHODS USEPA SW846 7470A and 245.1 CLP-M 4.1 (NJDEP does not accept CLPILM 04.1 after June, 2003), Addendum for USEPA CLP ILM 05.2

SOP NUMBER: **SOP-103**

REVISION NUMBER: **13**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: **07/20/06**

DATE OF LAST REVIEW **04/10/08**

MERCURY ANALYSIS IN WATER BY MANUAL COLD VAPORReferences:
SW846 Method 7470A
USEPA Method 245.1
USEPA SOW ILM04.1
See Addendum for SOW ILM05.2

I. SCOPE AND APPLICATION

A. This method is a cold-vapor atomic absorption procedure for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. This method can also be used for sludge-type wastes. All samples must be subjected to an appropriate dissolution procedure prior to analysis.

B. In addition to inorganic forms of mercury, organic materials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenol mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.

C. The range of the method may be varied through instrument and/or recorder expansion. Using a 30 mL sample, a detection limit of 0.2 µg Hg/L can be achieved.

II. SUMMARY OF METHOD

A. The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of a flow injection Mercury system. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

III. SAMPLE HANDLING AND PRESERVATION

A. Samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection, and refrigeration to 4°C.

B. The holding time for the mercury digestion is 28 days from time of sampling.

IV. INTERFERENCES

A. Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

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

C. Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 6.25 mL in 30 mL of sample). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by using an excess of hydroxylamine sulfate reagent (6.25 mL to 30 mL of sample).

D. Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized of organic mercury will be low. The problem can be eliminated by reducing the sample volume or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

V. Safety

A. Normal accepted laboratory practices should be followed while performing this procedure.

B. The toxicity and carcinogenicity of each reagent in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Normal accepted laboratory practices should be followed during reagent preparation and instrument operation. Always wear safety glasses or full-face shield for eye protection when working with these reagents. Each laboratory is responsible for maintaining a current safety plan, a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.

C. Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

D. The analyst should make sure that the system is vented to fresh permanganate in a bottle located at the back. Otherwise Hg vapors could be vented to the room.

VI. EQUIPMENT/APPARATUS

A. Perken Elmer Flow injection Mercury system

B. Mod Block Digester set to maintain 95±2°C for 2 hours.

C. Polypropylene sample digestion vessels with snap or screw caps or equivalent. **Five vessels of each lot of digestion vessels must be taken through analysis to check for mercury.**

VII. REAGENTS AND STANDARD PREPARATION

A. REAGENTS

1. Concentrated sulfuric acid suitable for Hg determination.

2. Concentrated nitric acid suitable for Hg determination.

3. Stannous chloride: in a 1000 mL volumetric flask add approximately 500 mL D.I. water, 30 mL concentrated HCl, add 11 grams stannous chloride crystals swirl to mix and dilute to 1000 mLs. Prepare fresh daily.

4. 3% HCl Carrier Solution: Dilute 30 mL of concentrated metals grade HCl to one liter. Prepare fresh daily.

5. Sodium chloride-hydroxylamine chloride solution: dissolve 120 grams of sodium chloride and 120 grams of hydroxylamine hydrochloride (very high grade --Do not get from Tennessee Reagents) in D.I. water and dilute to 1 liter. Note: this is normally made up 2 Liters at a time.

5. Potassium permanganate: 5% solution, w/v: dissolve 200 grams of potassium permanganate in 4000 mL of D.I. water. Should have "suitable for mercury determination" written on the side of the potassium permanganate bottle. This reagent takes overnight stirring (minimum of 3 hours if absolutely necessary). Use stirring bar already in the reagent bottle for this purpose. It is very easy to contaminate with mercury.

6. Potassium persulfate: 5% solution, w/v: dissolve 100 grams of potassium persulfate in 2000 mL D.I. water. Slight heating with stirring may be necessary to completely dissolve. The formation of crystals in this solution is not a problem.

B. STANDARDS

1. Traceability

a. A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

b. All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, and expiration date. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

c. The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

NOTE: All standard solutions should be prepared using class A volumetric flasks, class A volumetric pipettes (or calibrated Eppendorfs). All standards, blanks, and samples are taken through the digestion process.

a. Stock mercury solution: (100 µg/mL). Order from manufacturer already prepared. This solution is given a unique identifier.

b. Primary source and secondary source mercury standard solutions at 200 ug/L: dilute 2 mL of stock solution to 1000 mL in a 1000 mL volumetric flask, with 1.5 mL concentrated HNO_3.

c. Calibration standards

i. Prepared from the primary source working standard. The preparation of the calibration standards, etc. is described below.

a. Dilute the volumes below to 30 mLs in a 70 mL polypropylene vessel. (Note: The standards are diluted to 10 mLs for the initial step of the digestion. From that point when 25 mLs of DI water are added to samples, 15 mLs of DI water is added to the standards.

ug/L Hg	mLs of 200 ug/L standard in 30 mLs
0.20	0.03
0.50	0.075
1.0	0.15
2.0	0.30
4.0	0.60
6.0	0.90
10.0	1.5

iii. Appropriate reagents are added as below in the sample preparation section.

iv. Prepare one vessel for each.

v. It is necessary to digest the calibration standards.

e. Calibration verification standards

i. Initial calibration verification (ICV) solution – 4.0 ug/L

a. Prepared by diluting 0.6 mL of the second source standard to 30 mL with reagent water in a 70 mL polypropylene vessel. (TV = 4.0 ug/L)

b. Appropriate reagents are added as below in the sample preparation section.

c. It is necessary to digest the ICV standards for Method 7470A, Method 245.1 does not require digestion of standards.

ii. Continuing calibration verification (CCV) solution

a. Prepared from the primary source standard.

b. Prepared by diluting 0.3 mL of the primary standard at 200 ug/L to 30 mLs with reagent water in a 70 mL polypropylene vessel for 2.0 ug/L or 0.6 ml to 30 mls for 4.0 ug/L.

c. Appropriate reagents are added as below in the sample preparation section.

d. It is necessary to digest the CCV standards for Method 7470A, Method 245.1 does not require digestion of standards.

f. Digestion standards

i. Laboratory control sample

a. Prepared from the secondary source standard.

b. Prepared by diluting 0.3 mL of the second source standard to 30 mL with reagent water in a 70 mL polypropylene vessel.

c. Appropriate reagents are added as below in the sample preparation section.

d. This solution should be given a unique identifier in the digestion log.

ii.. Matrix Spikes

a. Prepared from the secondary source working standard.

b. Prepared by diluting 0.3 mL of the second source standard to 30 mL with sample in a 70 mL polypropylene vessel. Project specific or method specific requirements may over-ride the spiking level.

c. Appropriate reagents are added as below in the sample preparation section.

VIII. CALIBRATION

A. Set up the instrument with proper operating parameters.

1. Perkin Elmer Flow Injection Mercury System (FIMS).

i. Replace any old tubing that is around the pump cylinder. The sample transfer tubing connected to the seperator cover must not have any moisture in it. If it does replace it. **(Perkin-Elmer tygon**

tubing, waste and carrier 1.52mm I.D., waste only 3.17mm I.D., stannous chloride 1.14mm I.D.)

ii. Also replace the filter membrane with the rough side up. (for instructions refer to page 1-22 in maintenance manual.)

iii. Turn on PE 100 spectrophotmeter; (Note: this must be on in order to start up the software on the computer.)

iv. Turn on computer and go to icon "AA Win LAB Analyst".

v. Go to method; select "Hg CAL 2" then OK.

vi. Wavelength = 253.7; smoothing points =9; measurement = peak height; read time =18sec.; BCC time = 2 sec.

vii. Go to "Sample Info" and enter the order of the samples and other information that may be needed.

viii. Save entered sample list under "Save ….sample info file" Note: description and batch ID are normally the date of analysis.

ix. Go to "auto"; then to set-up. Select Browse in both spaces. One is to bring up your saved "Sample Information" File. The other is to select a results library. Double click on heading and choose.

x. Turn the printer on.

xi. Connect all tubing to the pump and blocks.

xii. Start the pump by going to "FIAS" and click the pump 1 Icon (120).

xiii. The pump will start, then lock down and tighten the tubes onto the pump.

xiv. Turn on the nitrogen tank, it should be above 500 psi on the guage. Replace the nitrogen tank when it is at 500 psi.

xv. The pressure gauge on the PE100 should be just below 100.

xvi. Use the tension adjuster to press down the tubing magazine to the pump head on the top and bottom. Start the pump and then lock them down. This technique needs to be demonstrated so that a new user will be able to understand what is needed here and how to do it.

xvii. Adjust the spring tension tubing until there is a constant "bubble of low rate" coming out to the waste tube.

xviii. Place carrier tubes into carrier and stannous chloride tube into SnCl2. (click valve fill inject and make sure flow is correct and the line is rinsed).

xix. Make sure the permanganate waste bottle is bubbling in order to absorb any Hg vapors which could be vented into the room.

xx. Allow a few minutes for reagents to flow through the system before starting analysis.

xxi. Calibrate: Go to "Auto" click on "Analyze", click on "calibrate".

xxii. "Select Location" enter #'s to be ran, and then press "OK". Samples are done in increments of 10 samples

B. Analyze the calibration standards as below.

1. New calibration points must be analyzed when the ICV analysis is not within ±10% for SW846-7470 or ± 5% for 245.1 methods. **A curve must be analyzed daily for all projects especially USACE and CLP projects.**

2. The curve should be linear with a calculated intercept with a minimum correlation coefficient (r) of ≥0.995 (USACE) or 0.998 (other). If not, a new curve must be analyzed.

IX. PROCEDURE

A. Glassware preparation

1. After use, samples are nuetralized and disposed down an acid sink with running water and rinsed with tap water. Or the sample may be discarded into the Mercury waste drum.

2. Wash mercury glassware in the dishwasher.

3. Acid clean the glassware used for mercury prep as follows:

   a. Rinse with low Hg content 1:1 HCl.

   b. Rinse with D.I. water.

B. Label the vessels indicating which sample will be in each..

C. Prepare calibration standards as detailed above. Add all reagents to the standards which are added to the samples as outlined below. Record the standard preparation in the digestion log.

D. Sample preparation

1. Transfer 30 mL, or an aliquot diluted to 30 mL of sample to the 30 mL mark on a 50 mL digestion vessel previously marked for this sample.

   NOTE: Normally, **a**n automatic dilution of 10X to 100X is performed for all TCLP extracts. All TCLP samples get one matrix spike unless several come in at one time from the same client with the same matrix. Then one in ten of the same matrix get spiked. Check with your manager.

2. Add 1.5 mL of concentrated sulfuric acid to each vessel and mix.

3. Add 0.75 mL of concentrated nitric acid to each bottle and mix.

4. Add 4.5 mL potassium permanganate solution to each vessel and mix. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate to the solution if necessary, until the purple color persists for at least 15 minutes (not more than 7.5 mL). If the purple color does not persist after the addition of 7.5 mL $KMnO_4$ the sample must be diluted prior to digestion. Inform your manager that the minimum detection limit cannot be reached for that particular matrix.

   NOTE: The same amount of $KMnO_4$ added to the samples should be present in the standards and blanks.

5. Add 2.4 mL of potassium persulfate to each vessel and mix. Cover.

6. Heat for 2 hours in the block digester at 95$\pm$2°C (the block temperature must be monitored and documented. Record observed temperature, correction factor, and the corrected temperature), cool.

6. Samples may be saved at this point if there is not time to run the whole set that day.

NOTE: Stannous Chloride (VII. A 5.) and 3% HCl (VII. A 8.) are added by the instrument during analysis.

E. Sample analysis

1. Set up the instrument as described in the calibration section above.

2. When ready to run samples, add 1.8 mL of sodium chloride-hydroxylamine chloride to reduce the excess permanganate. Sample analysis must be preceded by the analysis of an ICV with control limits of ±10% for SW846-7470 and ±5 % for 245.1. Followed by the ICB (< ±MDL for USACE or ±RL/CRDL for others and CLP).

3. Each set of ten samples and at the end of the analytical run must be followed by a CCV with control limits of ±20% for SW846-7470 and ±10% for 245.1

4. CCB must always follow the CCV. Control limits are (<±MDL for USACE or ±RL/CRDL for others and CLP). CCB must be run at the beginning and end of a sequence and after every 10 samples. **No analyte must be detected >2xMDL for DOD QSM Ver. 3.**

5. The autosampler log is set up to analyze 106 samples at a time.

Instrument Run Log example:

AS LOC	**Sample ID**
0	Wash
1	0.0
2	0.O2
3	0.05
4	0.1
5	0.2
6	0.4
7	0.6
8	1.0
9	ICV
10	ICB
11	LCSW
AS LOC	**Sample ID**
12	PBW
13	Sample
14	Sample
15	Sample
16	Sample
17	Sample
18	Sample
19	Sample
20	Sample

21	CCV
22	CCB
23	Sample
24	Sample
25	Sample
26	Sample
27	Sample
28	Sample
29	Sample
30	Sample
31	MS
32	MSD
33	FCV
34	FCB

F. Data reporting

1. Reduce data to result which will be reported.

2. Complete the data review checklist (attached). Must be completed and attached to each set of USACE data.

X. CALCULATIONS

A. Apply a least squares fit to the calibration standards plotting µg Hg/L versus the absorbance. For the concentration of the standards, assume 30 mL of solution volume (the 0.1 µg Hg standard will be input as 1.0 µg Hg/L) (0.1µg Hg / 0.030 L solution).

B. Input the sample absorbance into the mercury spreadsheet making sure that you are using the correct spreadsheet for the matrix of the sample.

C. Also make sure that the appropriate dilution factor is inputted in the correct space on the spreadsheet.

D. Report the data as µg Hg/L of sample.

XI. QUALITY CONTROL (Reference SW-846, 7470A Update III, USEPA CLP ILMO 4.1 or 245.1, Rev 3.0, 5/94 for further clarification)

A. Daily

1. **The instrument must be calibrated daily for all projects.**

2. Begin each analysis with an ICV. The control limits are ±10%.

3. Analyze ICB. Control limits (<±MDL for USACE or ±RL/CRDL for others and CLP)., depending on method. **No analyte detected >2xMDL for DOD QSM Ver. 3.**

4. If the ICV is not in control a new curve must be analyzed prior to sample analysis.

5. Follow each set of 10 samples with a CCV and also must end up with a CCV after the last sample. The control limits are ±20% for SW846-7470 and ± 10% for 245.1.

6. A CCB must always follow a CCV, the control limit is (<±MDL for USACE or ±RL/CRDL for others and CLP). CCB must be run at the beginning and end of a sequence and after every 10 samples. **No analyte detected >2xMDL for DOD QSM Ver. 3.**

B. Quarterly or as needed when doing straight CLP work.

1. IDL's for CLP 4.1.

C. Digestion

1. LCS data should be maintained and available for easy reference or inspection.

2. Preparation blank (<1/2 ±RL or ±RL/CRDL for common contaminates (USACE) and ±RL/CRDL for others and CLP).

   a. Employ a minimum of one preparation blank per sample batch to determine if contamination or any memory effects are occurring. The preparation blank is taken through the same digestion/preparation steps as the samples being tested. The result for the preparation blank must be below the method detection limit. If not, the analyst must use good judgment to evaluate the impact upon the associated samples. There is no impact if an associated sample is below the method detection limit nor if the level in the sample is greater than 10X the level found in the preparation blank. If the level of mercury in a sample is above the method detection limit but less than 10X the level found in the preparation blank, the sample must be redigested and reanalyzed or the data must be qualified on the final report. The project manager or QA manager will make this determination.

3. Laboratory control sample (LCS)

   a. Employ a minimum of one laboratory control sample (LCS) per sample batch to verify the digestion procedure. The LCS is taken through the same digestion/preparation steps as the samples being tested. The minimum control limits are ±20% for SW846-7470 and ±15% for 245.1. If the LCS is not in control, the impact upon the client data should be evaluated and the associated sample(s) should be either redigested or the data should be qualified. The project manager or QA Officer will make this determination.

D. Sample matrix

1. Analyze one replicate sample for every twenty samples. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. It is acceptable to substitute a matrix spike duplicate for the sample replicate. CLP does not allow this. Project specific requirements will take precedence in these situations.

2. Analyze one spiked sample and spiked sample duplicate for every twenty samples. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. Project specific requirements will take precedence in these situations. CLP requires 1 duplicate and 1 spike per batch. If the analyte level in the sample is not greater than four times the spiking level, the spike recoveries should be within ±25% of the true value. If not, check with supervisor to determine appropriate action. The final analytical report must document this situation.

   NOTE: For TCLP extracts, a matrix spike must be performed for each different matrix. The method of standard additions must be used if the sample spike recovery is not at least 50% and the concentration of Hg does not exceed the regulatory level and if the concentration of Hg measured in the extract is within 20% of the regulatory level.

3. The relative percent difference (RPD) between replicate determinations is to be calculated as referenced in the laboratory QA manual. (A control limit of ± 20% RPD shall be used for sample values greater than ten times the instrument detection limit.) Supervisor must be notified if the control limit is not met. Supervisor will determine corrective action if required. The final analytical report must document this situation.

4. For 245.1 analyze one serial dilution (1 to 5 dilution) for every 20 samples or per analytical batch, whichever is more frequent. Percent recovery

should be ±10%. The concentration of the original sample should be a minimum of 50X the IDL in order to apply the recovery criterion; if not, the serial dilution approach is not used.

5. When the sample matrix is so complex that viscosity, surface tension, and components can not be accurately matched with standards, the method of standard addition (MSA) is recommended. Section 8.6 of SW846-7000A provides tests to evaluate the need for using the MSA.

E. Method Detection Limit (MDL), Empirical Laboratories' Reporting Limit (ERL), Contract Required Quantitation Limit (CRQL) and Analyte Wavelength:

TABLE I

Aqueous Method Detection Limits(MDL), Empirical Laboratories' Reporting Limits(ERL), CLP OLM04.1 & OLM05.2 Contract Required Quantitation Limits (CRQL)				
Mercury by EPA 245.1, 7470A, SOW 4.1 & 5.2	**AQUEOUS MDL(ug/L)**	**AQUEOUS ERL(ug/L)**	**AQUEOUS CRQL ILMO 4.1 (ug/L)**	**AQUEOUS CRQL ILMO 5.2 (ug/L)**
Mercury	0.06081	0.20	0.2	0.2

TABLE 2

ANALYTE	**WAVELENGTH**
Mercury	**253.7**

XII. CORRECTIVE ACTIONS

A. INSTRUMENT RELATED

1. ICV not within ± 10% for SW846 and ±5% for 245.1
   a. If the problem is with the solution.
      i. Reprepare, obtain new stock if necessary.
   b. If the problem is with the calibration.
      i. Recalibrate through analysis of appropriate standards and recheck ICV.
2. CCV not within ± 20% for SW846 and ±10% for 245.1
   a. If the problem is with the solution.
      i. Reprepare, obtain new stock if necessary.
   b. If the problem is with the calibration.
      i. Recalibrate through analysis of appropriate standards and reprepare/reanalyze the previous ten sample according the following guidelines.
         a. If the CCV was biased high, any of the previous ten samples which were below the detection limit do not require reanalysis.
         b. If the CCV was biased low, the previous ten samples must be reanalyzed.

B. DIGESTION RELATED

1. The preparation blank less than ±1/2 RL or ±RL/CRDL for common contaminates (USACE) and ±RL/CRDL for others and CLP.

   a. If the problem is with the instrument or stannous chloride.
      i. Analyze a reagent blank to determine the stannous chloride and the instrument are behaving properly. If this check has detectable mercury, reprepare the stannous chloride or determine if there are any problems with the instrument. Contact supervisor immediately.

   b. If the problem is with the digestion.
      i. All associated samples which are below the RL, CRDL or have a level of mercury greater than 5X the level found in the preparation blank can be reported. If the level of mercury in an associated sample is not BMDL nor greater than 5X the level found in the preparation blank, the sample must be redigested/reanalyzed or reported as qualified. The project manager or QA manager will make this determination.

2. LCS not within control limits (or ±20%).
   a. If the problem is with the instrument.
      i. Reanalyze when instrument is in control if further sample bottles are available.
   b. Is the problem is with the digestion.
      i. If biased low, associated samples must be redigested.
      ii. If biased high, the impact upon the data user must be evaluated. The samples will be redigested or the data will be qualified on the final report.

C. SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20%
   i. The associated sample data must be qualified on the final report.

2. Spike analysis recovery not within ±25%
   i. If the analyte level in the sample is greater than 4X the spiking level, the %recovery can not be evaluated and no action is taken.
   ii. If the analyte level in the sample is not greater than 4X the spiking level, the associated sample data must be qualified on the final report. TCLP extracts must be evaluated as in section XI.D.2 above. The associated sample data must be qualified on the final report.

3. When the sample matrix is so complex that viscosity, surface tension, and components can not be accurately matched with standards, the method of standard addition (MSA) is recommended. Section 8.6 of SW846-7000A provides tests to evaluate the need for using the MSA.

XIII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area.
Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIV. REFERENCES

1. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846; Third Edition (Update III)*; Method 7470A

2. USEPA *Code of Federal Requlations, 40, CH 1,PT 136;* Method 245.1; APX-B

3. USEPA *Contract Laboratory Program(CLP) for Inorganics ILM04.1; ILM05.2*

XV. DEFINITIONS

1. Refer to SOP-431 for common definitions.

ADDENDUM FOR USEPA SOW ILM05.2

1. The CCV concentration must be different from the ICV.
2. The same CCV shall be used throughout analysis for an SDG.
3. Calibration standards must be within 5% of the standard concentration.
4. A CRA must be analyzed after the ICV/ICB and after each batch of 20 samples, but before the final CCV/CCB. The control limit is ±30%.
5. Spike samples at 1 ug/L for water.

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):	
Batch Number(s):	
Method:	**7470A (Mercury)**

QA/QC Item	Yes	No	NA	Second Level Review
1. Were samples analyzed within USACE holding times?				
2. Was initial calibration curve QC criteria met?				
3. Was all continuing calibration criteria in control?				
4. Did any sample exceed the highest calibration standard? (If yes, were appropriate dilutions made to generate samples concentration within calibration range?)				
5. Did LCS or blank spike meet control limits?				
6. Did MS/MSD meet control limits?				
7. Was the preparation (Method) Blank below the project required detection limits?				
8. Did you return samples back to cold storage immediately after use?				
9. Was water bath temperature monitored/documented and did you apply the thermometer correction factor?				
10. Sample preparation information is correct and complete.				
11. Analytical results are correct and complete.				
12. The appropriate SOP's have been used and followed.				
14. "Raw data" including all manual integration's have been correctly interpreted.				
15. "Special" sample preparation and analytical requirements have been met.				
16. Documentation complete (e.g., all anomalies in the analytical sequence have been documented, corrective action forms are complete.				

Comments on any "No" response:

_____
_____
_____
_____
_____
_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

MERCURY ANALYSIS IN SOIL/SEDIMENT BY MANUAL COLD VAPOR TECHNIQUE

METHODS SW846 7471A, 245.5 and CLPILM 04.1 (NJDEP does not accept CLPILM 04.1 after June, 2003), Addendum for USEPA CLP ILM 05.2

SOP NUMBER: **SOP-104**

REVISION NUMBER: **15**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: **04/10/08**

DATE OF LAST REVIEW **04/10/08**

MERCURY ANALYSIS IN SOIL/SEDIMENT BY MANUAL COLD VAPOR TECHNIQUE

References:
SW846 Method 7471A
USEPA Method 245.5, CLP SOW ILM04.1
See Addendum for CLP SOW ILM05.2

I. SCOPE AND APPLICATION:

A This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials.

B. The range of the method is 0.2 to 2 µg/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

II. SUMMARY OF METHOD:

A. A weighed portion of the sample is acid digested for 2 minutes at 95±2°C, followed by oxidation with potassium permanganate and with a secondary digestion at 95°C for 30 minutes. Mercury in the digested sample is then measured by the conventional cold vapor technique.

III. SAMPLE HANDLING AND PRESERVATION:

A. Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the lab that may result in contact with solid, liquid or airborne mercury.

B. Refrigerate solid samples at 4°C (±2°C) upon receipt until digestion and analysis.

C. The sample should be analyzed without drying. A separate percent solids determination is required

D. The holding time for digestion of mercury samples is 28 days.

IV. INTERFERENCES:

A. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

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

C. Samples high in chlorides require additional permanganate (as much as 12.5 mLs) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell.

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

V. SAFETY

A. Normal accepted laboratory practices should be followed while performing this procedure.

B. The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Always wear safety glasses or full-face shield for eye protection when working with these reagents. Each laboratory is responsible for maintaining a current safety plan, a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.

C. Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analyses should be conducted in a laboratory exhaust hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

VI. EQUIPMENT/APPARATUS:

A. Perkin Elmer Flow Injection Mercury System (FIMS)

B. Perkin Elmer AS 90

C. Mercury lamp

D. Environmental Express Mod-Block digestion block capable of holding 95±2°C for 2 hours

E. A scale or balance capable of weighing to 0.01 ± 0.02 gram.

F. Snap cap digestion polypropylene vessels for use with the mod block digester. **Five vessels of each lot must be taken through analysis to check for mercury**

G. Polypropylene watch glasses suitable for use with the above vessels in F above.

H. Manual Sample Mill

I. Wiley Sample Mill

J. Clippers for cutting vegetation

VII. REAGENTS AND STANDARD PREPARATION:

A. REAGENTS

1. Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

2. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3. Both HNO_3 and HCl must be of the reagent grade suitable for mercury determinations.

   NOTE: This reagent is required for use when USACE project samples are being digested.

3. Concentrated HCl.

4. Concentrated HNO_3.

5. Stannous chloride in a one liter volumetric flask add ~500 mL D.I. H_2O, 30 mL concentrated HCl, and 11g stannous chloride crystals. Swirl to mix and dilute to 1 L.

6. Sodium chloride-hydroxylamine chloride solution: Dissolve 120 g of sodium chloride and 120 g of hydroxylamine sulfate in reagent water and dilute to 1 L. Note : this is normally made up 2 liters at a time.

7. Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 200 g of potassium permanganate in 4 L of reagent water.

8. 3 % HCl carrier solution: 30 mL HCl – 1 L DI H20; Prepare fresh daily.

9. Potassium persulfate 5% solution: Dissolve 100g in 2 liters of D.I. water. Used with digestion of CLP soils.

B. STANDARDS

1. Traceability

a. A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

b. All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

c. The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

2. Preparation

NOTE: All standard solutions should be prepared using class A volumetric flasks, class A volumetric pipettes (or calibrated Eppendorfs). All Standards, blanks, and samples are taken through the digestion process.

a. Stock mercury solution: (100 µg/mL). Order from manufacturer already prepared. This solution is given a unique identifier.

b. Primary source and secondary source mercury standard solutions: dilute 2 mL of stock solution to 1000 mL in a 1000 mL volumetric flask, with 1.5 mL concentrated HNO_3 (200 ug/L).

c. Calibration standards

   i. Prepared from the primary source standard. The preparation of the calibration standards, etc. is described below.

      a. Dilute the volumes below to 5 mLs in a 70 mL polypropylene vessel. (Note: The standards are diluted to 5 mLs for the initial step of the digestion.)

ug/L Hg	mLs of 200 ug/L standard in 50 mL
0.20	0.050
0.50	0.125
1.0	0.25
2.0	0.50
4.0	1.0
6.0	1.5
10.0	2.5

   ii. Appropriate reagents are added as below in the sample preparation section.

   iii. Prepare one vessel of each.

   iv. It is necessary to digest the calibration standards when following all mercury methods.

e. Calibration verification standards

   i. Initial calibration verification (ICV) solution – 4.0 ug/L

      a. Prepared from the secondary source mercury standard (200 ug/L).

      b. Prepared by diluting 1.0 mL of the second source mercury standard to 5 mLs in a polypropylene digestion vessel.

      c. Appropriate reagents are added as below in the sample preparation section.

d. It is necessary to digest the ICV standards when using all mercury methods for soil.

ii. Continuing calibration verification (CCV) solution

a. Prepared from the primary or secondary source mercury standard. The concentration is alternated from 2.0 ug/L to 4.0 ug/L every 20 samples.

b. Prepared by diluting 0.50 for a 2.0 ug/L and 1.0 mL for a 4.0 ug/L of the secondary 200 ug/L standard to 5.0 mL with reagent water in a polypropylene digestion vessel.

c. Appropriate reagents are added as below in the sample preparation section.

d. It is necessary to digest the CCV standards when following all mercury methods for soil.

f. Digestion standards

1. Laboratory control sample

a. The Laboratory Control Sample (LCS) is prepared from the secondary source mercury standard (200 ug/L) and added to ~ 0.3 grams of teflon chips.

b. Prepared by diluting 0.50 mL of the secondary mercury standard (200 ug/L) to 5 mLs in a polypropylene digestion vessel with 0.30 grams of teflon chips.

c. Appropriate reagents are added as below in the sample preparation section.

d. This solution is given a unique identifier in the digestion log.

2. Matrix Spikes

a. Prepared from the primary or secondary source mercury standard (200 ug/L).

b. Prepared by adding 0.50 mL of the mercury standard (200 ug/L) to the sample in a polypropylene digestion vessel. Project specific requirements may over-ride the spiking level.

c. Appropriate reagents are added as below in the sample preparation section.

VIII. CALIBRATION:

A. Set up the instrument with proper operating parameters.

1. Perkin Elmer Flow Injection Mercury System (FIMS)

a. Prepare the instrument for calibration by the following steps:

i. Replace any old tubing that is around the pump cylinder. The sample transfer tubing connected to the seperator cover must not have any moisture in it. If it does replace it. **(Perkin-Elmer tygon tubing, waste and carrier 1.52mm I.D.,waste only 3.17mm I.D., stannous chloride 1.14mm I.D.)**

ii. Also replace the filter membrane with the rough side up. (for instructions refer to page 1-22 in maintenance manual.)

iii. Turn on PE 100 spectrophotometer; (Note: this must be on in order to start up the software on the computer.)

iv. Turn on computer and go to icon "AA Win LAB Analyst"

v. Go to method; select "Hg CAL 2" then OK.

vi. Wavelength = 253.7; smoothing points =9; measurement = peak height; read time = 18 sec.; BCC time = 2 sec.

vii. Go to "Sample Info" and enter the order of the samples and other information that may be needed.

viii. Save entered sample list under "Save …sample info file" Note: description and batch ID are normally the date of analysis.

ix. Go to "auto"; then to set-up. Select Browse in both spaces. One is to bring up your saved "Sample Information." File. The other is to select a results library. Double click on heading and choose.

x. Turn the printer on.

xi. Connect all tubing to the pump and blocks.

xii. Start the pump by going to "FIAS" and click the pump 1 Icon (120).

xiii. The pump witll start, then lock down and tighten the tubes onto the pump.

xiv. Turn on the nitrogen tank, it should be >500 psi on the guage. Replace the nitrogen tank when it is at 500 psi.

xv. The pressure gauge on the PE100 should be just below 100.

xvi. Use the tension adjuster to press down the tubing magazine to the pump head on the top and bottom. Start the pump and then lock them down. This technique needs to be demonstrated so

that a new user will be able to understand what is needed here and how to do it.

xvii. Adjust the spring tension tubing until there is a constant "bubble of low rate" coming out to the waste tube.

xviii. Place carrier tubes into carrier and stannous chloride tube into SnCl2. (click valve fill inject and make sure flow is correct and the line is rinsed)

xix. Make sure the permanganate waste bottle is bubbling in order to absorb any Hg vapors which could be vented into the room.

xx. Allow a few minutes for reagents to flow through the system before starting analysis.

xxi. Calibrate: Go to "Auto" click on "Analyze", click on "calibrate".

xxii. "Select location" enter the #'s of the samples to be analyzed, then "OK".

B. Analyze the calibration standards as below.

1. A curve must be analyzed daily for all projects. A new curve must be analyzed when the ICV analysis is not within ±10% for SW846 7471 or ±5% for 245.5 methods.

2. The curve should be linear with a calculated intercept with a minimum correlation coefficient(r) of ≥0.995 (USACE) or 0.998 (other). If not, a new curve must be analyzed.

3. **CLP requires a blank + 5 calibration standards (0, .02, .05, .1, .5 and 1.0 µg). (One standard must be at CRDL or IDL whichever is greater.)**

IX. PROCEDURE:

A. Prepare calibration standards as detailed above. Add all reagents to the standards which are added to the samples as outlined below. Record the standard preparation in the standard log.

B. Sample preparation

It is extremely important that waste (when appropriate), soil and sediment samples be mixed thoroughly to ensure that the sample is as representative as possible of the sample media. The most common method of mixing is referred to as quartering. The quartering procedure should be performed as follows:

- The material in the sample pan(inorganic-plastic/organic-aluminum) should be divided into quarters and each quarter should be mixed individually.

- Two quarters should then be mixed to form halves.
- The two halves should be mixed to form a homogenous matrix.

This procedure should be repeated several times until the sample is adequately mixed.

NOTE: Samples that are clay type materials must be handled in a different manner. Due to these type sample matrices having an affinity to stick to most anything that touches it, another approach must be followed. Obtain a representative sub-sample aliquot from the center or middle section of the sample container.

Grinding of Vegetation Samples

Remove sample from shipping container and brush off dirt particles. Chop sample into about half inch pieces with clippers or other cutting tool. Place the sample in an aluminum pan and air-dry in an exhaust hood to the appropriate dryness for grinding. It should be dry enough where it won't stick to the inside of the mill. Grind the dried sample to fineness in either the manual sample mill or the Wiley mill or both if needed. Place the ground sample in a container and label immediately.

1. Transfer 0.30 g (for USACE work use anywhere from 0.20 to 1.0 g and record the weight in the digestion log) of sample to a polypropylene digestion vessel previously marked for this sample. Record the exact sample mass on the bottle and in the digestion log. (Note: the balance must be calibrated for the specific task. Calibrate by weighing a 0.5 and a 0.1g weight on the balance along with a digestion vessel. Record in specific balance calibration log.)

2. Add 2.5 mL of reagent water, and 2.5 mL of aqua regia and mix for samples. Add 2.5 mL of aqua regia to standards and mix.

3. Cover samples and standards with watch glasses and heat for 2 minutes in the hot block at 95$\pm$2°C (The hot block temperature must be monitored and documented. Record observed temperature, correction factor, and the corrected temperature).

4. Cool, bring to 30 ml with D.I. water

5. Add 7.5 mL potassium permanganate solution to each vessel and mix. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate to the solution if necessary, until the purple color persists for at least 15 minutes (not more than 12.5 mL).

NOTE: The same amount of $KMnO_4$ added to the samples should be present in the standards and blanks.

6. Heat for 30 minutes on the hot block at 95±2°C (The temperature must be monitored and documented. Record observed temperature, correction factor, and the corrected temperature), cool. Samples may be saved at this point if there is not time to run the whole set that day.

7. Add 3 mLs of sodium chloride-hydroxylamine chloride solution to each vessel.

8. Bring to 50 ml with D.I. water both standards and samples. Cap mix and vent to decolor and release Cl gas. The samples are now ready for analysis.

NOTE: Stannous Chloride (VII. A 5.) and 3% HCl (VII. A 8.) are added by the instrument during analysis.

C. Sample analysis

1. Set up the instrument as described in the calibration section above.

2. When ready to run samples, transfer samples and standards to autosampler tubes and load the auto sampler according to the sample information sheet set up previously. If chlorides are suspected, purge the head space in the polyethylene tube for at least 1 minute to get rid of any chlorine gas collected there. After a delay of at least 30 seconds the sample is ready for step "3". **NOTE:** When aqua-regia is added assume that all samples and standards have chlorine and treat accordingly. Purging the samples of chlorine is accomplished by putting a pasteur pipette on the end of some air tubing hooked to a fish pump. The pasteur pipette is then placed at an angle into the top of the polyethylene vessel without breaking the surface of the sample. It takes about one minute to purge the air above the sample of chlorine.

3. Analysis must be preceded by the analysis of an ICV (concentration at or near mid range) with control limits of ±10% for SW846-7471A and ±5% for 245.5 methods.

4. The ICB must follow the calibration standards (<±MDL (USACE) or ±RL/CRDL for other or CLP), but not before the ICV. **No analyte must be detected > 2xMDL for DOD QSM Ver. 3.**

5. Each set of ten samples must be followed by a CCV with control limits of ±20% for SW846-7471 and ±10% for 245.5 method. The run must also end with a CCV, then CCB.

6. Analyze CCB after calibration and each CCV. The CCB frequency is 10% or every 2 hours whichever is more frequent. (control limit is < ±MDL or ±RL/CRDL for other or CLP). **For DOD QSM Ver.3 CCB at beginning and end of sequence and after every 10 samples. No analyte detected > 2xMDL.**

7. Instrument Run Log example:

AS LOC	Sample ID
0	Wash
1	0.0
2	0.O2
3	0.05
4	0.1
AS LOC	**Sample ID**
5	0.2
6	0.4
7	0.6
8	1.0
9	ICV
10	ICB
11	LCSW
12	PBW
13	Sample
14	Sample
15	Sample
16	Sample
17	Sample
18	Sample
19	Sample
20	Sample
21	CCV
22	CCB
23	Sample
24	Sample
25	Sample
26	Sample
27	Sample
28	Sample
29	Sample
30	Sample
31	MS
32	MSD
33	FCV
34	FCB

8. Sample analysis:

   i. Go to "Analyze", "select location" and type in the range of numbers needed to complete analysis. (ie. 9-54). Press enter and the autosampler will proceed to enter the selected range. NOTE: Check standards are loaded as part of the tray.

   ii. Make sure that the sample wash beaker is filled with 3% HCl.

   iii. Dilute and reanalyze samples that are more concentrated than within 10% of the high standard. Soil sample dilutions are made from the digested aliquot. Sample concentration results that are below the calibration curve but above the MDL are reported flagged as estimated, ("B" flag).

D. Data reporting

1. Reduce data to result which will be reported using the soil spreadsheet found on the network..

2. Complete the data review checklist (attached). Must be completed and attached to each set of USACE data.

X. CALCULATIONS:

A. Pull up the blank spreadsheet at K:\wcm\tests\mercury and fill in all the information pertinent to the current analysis. Save as the date of analysis. This information can be obtained from your mercury digestion log.

B. Input the sample absorbance into the excel spreadsheet in the appropriate cell. The spreadsheet uses the current calibration to calculate the Hg results.

C. Make sure that the appropriate dilution factors are entered into the spreadsheet in the correct cells.

D. The spreadsheet should divide the result which is the µg Hg obtained from the sample mass by the sample mass in grams. This will yield a result of µg Hg/g sample on a wet weight basis. Calculations in the spreadsheet should be checked occassionally to make sure that they are working correctly.

E. If available, divide the result by the %solids to obtain the result on a dry weight basis.

F. Report the data as µg Hg/g of sample (mg/kg wet or mg/kg dry when % solids are available).

XI. QUALITY CONTROL (Reference SW-846, 7471A Update III, USEPA CLP ILMO 4.1 or EPA 245.5 for further clarification)

A. Daily

1. **The instrument must be calibrated daily for all projects.**

2. Begin each analysis with an ICV. The control limits are ±10% for 7471 and ±5% for 245.5.

3. Analyze ICB. Control limit is <± **MDL** or ±RL/CRDL for other or CLP. **For DOD QSM Ver. 3, no analyte detected > 2x MDL.**
4. If the ICV is not in control a new curve must be analyzed prior to sample analysis.

5. Follow each set of 10 samples with a CCV and also must end up with CCV after last sample. The control limits are ±20% for SW846-7471 and ±10%for 245.5. If an exceedance occurs, analyze another CCV, if the second CCV fails, then a new calibration curve should be generated and all affected samples should be reanalyzed.

6. Follow each CCV with a CCB. Control limit is **< ±MDL** or ±RL/CRDL for others or CLP. **For DOD QSM Ver. 3, no analyte detected > 2x MDL.**

B. Quarterly

1. IDLs for CLP (Follow SOP - 414).

C. Annually

1. MDLs must be analyzed for all matrixes (Follow SOP - 414).

D. Digestion

1. LCS data should be maintained and available for easy reference or inspection.

2. Preparation blank (< ±½ RL or ±RL for common contaminates or ±RL/CRDL for others or CLP)

a. Employ a minimum of one preparation blank per sample batch to determine if contamination or any memory effects are occurring. The preparation blank is taken through the same digestion/preparation steps as the samples being tested. The result for the preparation blank must be < ± ½ RL for USACE or ±RL/CRDL for others or CLP. If not, the analyst must use good judgment to evaluate the impact upon the associated samples. There is no impact if an associated sample is below the method detection limit or if the level in the sample is greater than 10X the level found in the preparation blank. If the level of mercury in a sample is above the method detection limit, but less than 10X the level found in the preparation blank, the sample must be redigested and reanalyzed or the data must be qualified on the final report. The project manager or QA officer will make this determination.

3. Laboratory control sample (LCS).

a. Employ a minimum of one LCS per sample batch to verify the digestion procedure.. The LCS is taken through the same digestion/preparation steps as the samples being tested. The minimum control limits are ±20% for SW846-7471 and ±15% for 245.5 solid samples. An LCS will accompany each batch of soil samples. If the LCS is not in control, the Inorganic Manager and QA Officer must be notified immediately. Several possibilities exist at this point and a thorough investigation and data evaluation is essential. The first question is to evaluate the impact upon the data. All samples may need to be retested or flagged with the appropriate qualifier. The next question is to find out why it occurred and to proceed with a corrective action plan to prevent reoccurrence. This corrective action is documented in a CAR.

E. Sample matrix

1. Analyze one replicate sample for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. It is acceptable to substitute a matrix spike duplicate for the sample replicate. Project specific requirements will take precedence in these situations.

2. Analyze one spiked sample and spiked sample duplicate for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. Project specific requirements will take precedence in these situations. CLP requires 1 duplicate and 1 spike per batch. If the analyte level in the sample is not greater than four times the

spiking level, the spike recoveries should be within ±25% of the true value. If results do not fall within the control limit-redigestion/reanalysis may be required. If reanalysis is not required, the associated batch of samples will be flagged accordingly. Discuss the situation with your supervisor. A Corrective Action Report (CAR) must be filled out and attached to the data as well as emailed or sent to the supervisor when the control limits are exceeded.

3. The relative percent difference (RPD) between replicate determinations is to be calculated as referenced in the laboratory QA manual. (A control limit of ± 20% RPD (non-aqueous samples may routinely exceed this amount) shall be used for sample values greater than ten times the instrument detection limit.) Supervisor must be notified if the control limit is not met. Supervisor will determine corrective action if required. The final analytical report must document this situation. A Corrective Action Report (CAR) must be filled out and attached to the data as well as emailed or sent to the supervisor when the control limits are exceeded.

4. For 245.5 analyze one serial dilution (1 to 5 dilution) for every 20 samples or per analytical batch, whichever is more frequent. Percent recovery should be 10%. The concentration of the original sample should be a minimum of 50X the IDL in order to apply the recovery criterion; if not, the serial dilution approach is not used.

5. When the sample matrix is so complex that viscosity, surface tension, and components can not be accurately matched with standards, the method of standard addition (MSA) is recommended. Section 8.6 of SW846-7000A provides tests to evaluate the need for using the MSA.

F. Method Detection Limit (MDL), Empirical Laboratories' Reporting Limit (ERL), Contract Required Quantitation Limit (CRQL) and Analyte Wavelength:

TABLE I

Solid/Soil Method Detection Limits(MDL), Empirical Laboratories' Reporting Limits(ERL), CLP OLM04.1 & OLM05.2 Contract Required Quantitation Limits (CRQL)				
Mercury by EPA 245.1, 245.5, 7471A, SOW 4.1 & 5.2	**SOLID/SOIL MDL (mg/Kg)**	**SOLID/SOIL ERL (mg/Kg)**	**SOLID/SOIL CRQL ILMO 4.1 (mg/Kg)**	**SOLID/SOIL CRQL ILMO** 5.2 (mg/Kg)
Mercury	0.0157	0.033	0.1	0.1

TABLE 2

ANALYTE	WAVELENGTH
Mercury	253.7

XII. CORRECTIVE ACTIONS

A. INSTRUMENT RELATED

1. ICV not within ± 10% (SW846) or ± 5% (245.5)
   a. If the problem is with the solution.
      i. Reprepare, obtain new stock if necessary.
   b. If the problem is with the calibration.
      i. Recalibrate thru analysis of appropriate standards and recheck ICV.

2. CCV not within ± 20% (SW846) or ±10% (245.5)
   a. If the problem is with the solution.
      i. Reprepare, obtain new stock if necessary.
   b. If the problem is with the calibration.
      i. Recalibrate thru analysis of appropriate standards and reprepare/reanalyze the previous ten sample according the following guidelines.
         a. If the CCV was biased high, any of the previous ten samples which were below the minimum detection limit do not require reanalysis.
         b. If the CCV was biased low, the previous ten samples must be reanalysed.

B. DIGESTION RELATED

1. The preparation blank less than ± ½ RL for USACE or ±RL/CRDL for others or CLP.
   a. If the problem is with the instrument or stannous chloride.
      i. Analyze a reagent blank to determine the stannous chloride and the instrument are behaving properly. If this check has detectable mercury, reprepare the stannous chloride or determine if there are any problems with the instrument.
      ii. If the problem was with the instrument or the stannous chloride and the situation is corrected continue analysis with a second aliquot of the preparation blank.
   b. If the problem is with the digestion.
      i. All associated samples which are below the method detection limit (MDL) or have a level of mercury greater than 10X the level found

in the preparation blank can be reported. If the level of mercury in an associated sample is not <MDL nor greater than 10X the level found in the preparation blank, the sample must be redigested/reanalyzed or reported as qualified. The project manager or QA manager will make this determination.

2. LCS not within control limits.
   a. If the problem is with the instrument.
      i. Reanalyze when instrument is in control with another aliquot of the sample.
   b. If the problem is with the digestion.
      i. If biased low, associated samples must be redigested.
      ii. If biased high, the impact upon the data user must be evaluated. The samples will be redigested or the data will be qualified on the final report.

C. SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20%
   i. The associated sample data must be qualified on the final report.
2. Spike analysis recovery not within ±25%
   i. If the analyte level in the sample is greater than 4X the spiking level, the %recovery can not be evaluated and no action is taken.
   ii. If the analyte level in the sample is not greater than 4X the spiking level, the associated sample data must be qualified on the final report. A corrective action report must accompany the data and be emailed or given to the superviser.

XIII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area.

Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIV. REFERENCES

1. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846; Third Edition (Update III)*; Method 7471A

2. USEPA *Code of Federal Requlations, 40, CH 1,PT 136;* Method 245.1; APX-B

3. USEPA *Contract Laboratory Program(CLP) for Inorganics ILM04.1; ILM05.2*

XV. DEFINITIONS

1. Refer to SOP-431 for common definitions.

Addendum for USEPA CLP ILM 05.2

1. CCV concentration must be different from ICV.

2. The same CCV shall be used throughout analysis for a sample delivery group.

3. Calibration standards must be within 5% of the standard concentration.

4. 0.2 grams of sample must be used for the sample aliquot, add enough reagent water to each sample to make a total volume of 10 mL. Proceed with method as in the water method SOP 103.0 Revision 9.

5. The ICV and CCV must be at ±20% recovery.

6. A CRA must be analyzed at the beginning and end of each batch of 20 samples. Right after the ICV/ICB and right before the final CCV/CCB. The control limit is ±30%.

7. The matrix spike must be analyzed at the concentration of 0.5 mg/Kg.

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):
Batch Number(s):
Method: 7471A (Mercury)

QA/QC Item	Yes	No	NA	Second Level Review
1. Were samples analyzed within USACE holding times?				
2. Was initial calibration curve QC criteria met?				
3. Was all continuing calibration criteria in control?				
4. Did any sample exceed the highest calibration standard? (If yes, were appropriate dilutions made to generate samples concentration within calibration range?)				
5. Did LCS or blank spike meet control limits?				
6. Did MS/MSD meet control limits?				
7. Was the preparation (Method) Blank below the project required detection limits?				
8. Did you return samples back to cold storage immediately after use?				
9. Was water bath temperature monitored/documented and did you apply the thermometer correction factor?				
10. Sample preparation information is correct and complete.				
11. Analytical results are correct and complete.				
12. The appropriate SOP's have been used and followed.				
14. "Raw data" including all manual integration's have been correctly interpreted.				
15. "Special" sample preparation and analytical requirements have been met.				
16. Documentation complete (e.g., all anomalies in the analytical sequence have been documented, corrective action forms are complete.				

ANALYST DATA REVIEW CHECKLIST
7471A (Mercury)

Comments on any "No" response:

_____
_____
_____
_____
_____
_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

METALS ANALYSIS

BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY (ICP-AES) TECHNIQUE

METHODS 200.7, (SW846) 6010B, (SM 19th Edition 2340B) Hardness Calculation, (USEPA CLP) ILMO 4.1 (NJDEP does not accept CLPILM 04.1 after June, 2003)

Addendum for USEPA CLPILM 05.2

SOP NUMBER: **SOP-105**

REVISION NUMBER: **13**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: **04/10/08**

DATE OF LAST REVIEW: **04/10/08**

ICP METHOD
SOP
References: SW-846, Method 6010B, December 1996
USEPA, Method 200.7, June 1991, Standard Methods 19th Edition 2340B, 1995
USEPA CLP, ILM 04.1. See Addendum for USEPA CLPILM 05.2

I. SCOPE AND APPLICATION

A. Inductively Coupled Argon Plasma (ICP) determines trace elements in solution. **We use the ICP to determine the concentration of the following metals: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V and Zn.** All matrices, including ground water, aqueous samples, TCLP, SPLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

B. **Detection limits, sensitivity, and optimum ranges of the metals may be found in the ICP method file.** Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

II. SUMMARY OF METHOD

A. Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g., Methods 3005-3050 and SOW ILM 04.1/05.2). When analyzing for dissolved constituents, acid digestion is not always necessary if the samples are filtered and acid preserved prior to analysis. If particulates form after filtration and preservation the sample must be digested prior to analysis.

NOTE: When selenium is required soluble samples must always be digested.

B. This method describes the simultaneous multi-elemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analytic wavelength measured. Background correction is not required in cases of line

broadening where a background correction measurement would actually degrade the analytical result.

C. ICP's primary advantage is that it allows simultaneous determination of any elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and background correction to minimize these interferences, analysis for traces of metals in the presence of a large excess of a single metal is difficult. Examples would be traces of metals in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FAA.

D. It is standard procedure to use an internal standard (Yttrium) with samples to increase the stability of the instrument as recommended by the manufacturer (TJA). (When samples are suspected of containing Yttrium internal standard cannot be used.)

III. SAMPLE HANDLING AND PRESERVATION

A. Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Water samples which have been prefiltered and acidified will not need acid digestion as long as the samples and standards are matrix matched and particulates do not form after the filtration and preservation take place. Solubilization and digestion procedures are presented in Sample Preparation Methods (Methods 3005A-3050A).

B. Sample digestates are stored at room temperature for at least 2 months unless a longer time is requested by the client. The samples contain an acid matrix of 3:1. Since the most concentrated acid matrix allowed for direct disposal down an acid sink is a ratio of 20:1, the samples must be diluted with 1 part water to 2 parts sample prior to pouring down the sink while the tap water is running.

C. **The appropriate SOPs should be consulted regarding sample preparation.** The following is a brief summary of the methods we use for metals preparation.

- Method 3005A prepares groundwater and surface water samples for total recoverable and dissolved metals determination by ICP. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

- Method 3010A prepares waste samples for total metal determination by ICP. The samples are vigorously digested with a mixture of nitric acid and hydrochloric acid followed by dilution with laboratory water. The method is applicable to aqueous samples, TCLP and mobility-procedure extracts.

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- Method 3031 prepares oily waste samples for total metal determination by ICP. The samples are mixed with permanganate, H_2SO_4 , HNO_3, and HCl, then filtered. The filter is then added back to the filtrate and heated with more HNO_3 and filtered once again. If manganese is needed a manganese removal step is necessary.

- Method 3050B prepares waste samples for total metals determination by ICP. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either laboratory water or hydrochloric acid and laboratory water. The method is applicable to soils, sludges, and solid waste samples.

IV. INTERFERENCES

A. Spectral interferences are caused by background contribution from continuum or recombination phenomena, stray light from the line emission of high-concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

1. Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line interferences are handled by including spectra on interfering species in the algorithm.

2. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If

a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral intereference effects from all method anlytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using anlyte concentrations that will adequtetely describe the interfernce. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration , a more appropriate test would be to use a concentration near the upper analytical range limit.

3. Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelength are listed in the method in table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

4. When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2 from the method, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximatley 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interferences than that shown in Table 2 from the method. The interference effects must be evaluated for each individual instrument since the intensities will vary.

5. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of

dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an intefering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

6. The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and agron flow rate). When using the recommended wavelengths, the anlaylst is required to determine and document for each wavelength the effect from referenced interferences as well as any other suspected interferences that may be specific to the instrument of matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

7. If the correction routine is operating properly, the determined, apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adquate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

8. When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should e

inspected to ensure that there is no contamination that may be perceived as a spectral interference.

B. Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also it is has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers.

C. Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the elements and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

D. Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

V. SAFETY

A. Normal accepted laboratory safety practices should be followed while performing this analysis.

1. Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of appropriate safety gloves and lab coats is highly recommended.
2. Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples that need special consideration have applicable notes on the sample logs.
3. MSDS sheets are available for all reagents and standards that have been purchased. These are located in the bookshelves in the Quality Assurance Officers office.

VI. EQUIPMENT/APPARATUS

A. Inductively coupled argon plasma emission spectrometer: Thermo Jarrell Ash (TJA) 61E trace or equivalent.

B. Computer-controlled emission spectrometer with background correction: Thermo Jarrell Ashe (TJA) 61E trace or equivalent.

C. Radio frequency generator compliant with FCC regulations: TJA 61E trace or equivalent.

D. Argon gas supply – Liquid Argon

E. Class A volumetric flasks

F. Class A volumetric pipettes

G. Analytical balance - capable of accurate measurement to a minimum of three significant figures (.001gm): Mettler model AE100

H. Variable Eppendorf Pipettes 1000µL; 5000µL

VII. REAGENTS AND STANDARD PREPARATION

A. Notes

1. Reagent Water. All references to water in the method refer to reagent grade water unless otherwise specified. Reagent water will be interference free.

2. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

B. REAGENTS

1. Hydrochloric acid (concentrated), HCl.
2. Nitric acid (concentrated), HNO_3.

C. STANDARDS

1. Matrix

a. All standards contain 2% HNO_3 and 5% HCl.

2. Storage

a. The standards are stored at room temperature in 500 mL Teflon bottles.

3. Traceability

a. A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

b. All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date and the logbook where information is recorded. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.)

shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

c. The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

4. Calibration standards

a. All standards have an acid matrix of 2% HNO_3 and 5% HCl and should be prepared using class A volumetric flasks, class A volumetric pipettes (or calibrated Eppendorfs).

b. STD-1 is the calibration blank: Reagent grade water **matrix matched as in (a) above. Note: when this standard is analyzed the intensities should be compared to a previous run to make sure that no contamination has occurred. Prepare this solution fresh daily.**

c. Stock QC21 solution: (100 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier and includes the following metals - Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, Se, Sr, Tl, Ti, V, and Zn.

d. Stock Boron solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

e. Stock Tin solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

d. QC21 High (10 ug/mL). Dilute 50 mL of stock QC21 solution, 5 mL of stock Boron solution and 500 uL of stock Tin solution to 500 mL in a 500 mL volumetric flask, with 25 mL TRACE, Concentrated HCl and 10 mL TRACE, Concentrated HNO3. Prepare this solution fresh every three to six months.This standard is used to calibrate the following-As,B,Be,Cd,Co,Cr,Cu,Mn,Mo,Ni,Pb,Sb,Se,Sn,Ti,Tl,V,Zn.

e. Stock Silver solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

f. Stock Aluminum solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

g. Stock Calcium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

h. Stock Magnesium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

i. Stock Iron solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

j. Stock Potassium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

k. Stock Barium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

l. Stock Sodium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

m. NAK High solution: (500000 ug/L Al,Fe), (2000 ug/L Ag), (5000 ug/L Ba), (500 mg/L Mg). Dilute 25 mL stock Al, Fe, Mg; and 1 ml stock Ag solution; and 0.25 mL of stock Ba solution to 500 mL in a 500 mL volumetric flask with 25 mL TRACE, Concentrated HCl and 10 mL TRACE, Concentrated HNO3. Solution is stable for 6 months.

n. NAK 100ppm solution: (100 mg/L Ca, Na, K.) Dilute 5.0 mL stock Ca, Na, K solutions into a 500ml flask with 25 mL TRACE, Concentrated HCl and 10 mL TRACE, Concentrated HNO3. Solution is stable for 6 months.

o. Stock Arsenic solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

p. Stock Cobalt solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

q. Stock Chromium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

r. Stock Copper solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

s. Stock Manganese solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

t. Stock Nickel solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

u. Stock Lead solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

v. Stock Selenium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

w. Stock Thallium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

x. Stock Beryllium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

y. Stock Cadmium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

z. Stock Antimony solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

aa. Stock Molybdenum solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

bb. Stock Strontium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

cc. Stock Titanium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

dd. Stock Vanadium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

ee. Stock Zinc solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

ff. Stock Ultimate Low Standard: (200 µg/L Ag, As, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl); (2500 µg/L Al); (2000 µg/L Fe); (50 µg/L Be, Cd); (10 mg/L B, Sn, Ca, Mg); (500 µg/L Sb, Zn); (1000 µg/L Mo, Sr, Ba, Ti); (200 µg/L V). Dilute 100 uL of stock Ag, As, Co, Cr, Cu, Mn, Ni, Pb, Se, V and Tl solutions; 125 µ/L of stock Al solution; 100 uL of stock

Fe solution; 5 mL of stock B solution; 500 uL of stock Sn, Ca, and Mg solutions; 250 uL of stock Sb and Zn solutions; 500 uL of stock Mo, Sr, Ba and Ti solutions; 1.0 mL of stock Cd and Be diluted to 100 mL and then use 2.5 mL of that solution diluted to 500 mL in a 500 mL volumetric flask with 25 mL TRACE, Concentrated HCl and 10 mL TRACE, Concentrated HNO3. Solution is stable for 6 months.

gg. Ultimate Low Standard: (20 µg/L Ag, As, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl); (250 µg/L Al); (200 µg/L Fe); (5.0 µg/L Be, Cd); (1.0 mg/L B, Sn, Ca, Mg); (50 µg/L Sb, Zn); (100 µg/L Mn, Sr, Ba, Ti); (20 µg/L V). Dilute 10 mL of Stock Ultimate Low Standard to 100 mL in a 100 mL volumetric flask with 5 mL of TRACE, Concentrated HCl and 2 mL TRACE, Concentrated HNO3. This solution is prepared daily.

Stock Ultimate Low Standard and Ultimate Low Standard are only used when specified by client.

5. Calibration Verification standards

a. ICV Prep- 1.0 ml of QC-23, 1.0 ml of QC-7, 0.1 ml of 10,000 ppm Na, 0.09 ml of Fe at 10,000 ppm, and 0.09 ml of Al at 10,000 ppm diluted to 100 ml with 2% HNO3 and 5% HCL matrix. Mix well. CCV Prep- 1.0 ml of QC-21, 1.0 ml of QC-7, 1.0 ml of SN at 100 ppm, 0.1 ml of Na at 10,000 ppm, 0.09 ml of FE at 10,000 ppm,and 0.09 ml of Al at 10,000 ppm diluted to 100 ml with 2% HNO3 and 5% HCL matrix and mix well. This solution is prepared daily. These solutions are given a unique identifier and recorded in the standard log. ICV is prepared from a source independent from that used in the initial calibration.

b. The CRI solution is analyzed to check the accuracy of the instrument down near the contract required detection limits (CRDL). It is analyzed in conjunction with the interference check sample. The sample is prepared from a purchased solution which contains 120 µg/mL Sb, 100 µg/mL Co and V, 80 µg/mL Ni, 50 µg/mL Cu, 40 µg/mL Zn, 30 µg/mL Mn, 20 µg/mL As, Cr, Ag and Tl, 10 µg/mL Be, Cd and Se along with 6 µg/mL Pb. 500 µ/L of the solution is diluted to 500 mL. This solution is stable for 6 months.

b. The interference check solutions (ICSA and ICSAB) are prepared to contain known concentrations of interfering elements that will provide an adequate test of the IECs. A solution containing 500 ug/mL Al, Ca, Mg and 200 ug/mL Fe is diluted 10x to prepare the ICSA. The ICSAB is prepared by diluting 100x a solution containing 10 ug/mL of As and Tl; 20 ug/mL Ag; 50 ug/mL Ba, Be, Cr, Co, Cu, Mn, and V; 100 ug/mL Cd, Ni and Zn; 5 ug/mL Pb and Se; and 60 ug/L Sb. Add to this a solution containing 500 ug/mL Al, Ca, Mg and 200 ug/mL Fe diluted 10x. These solutions are prepared as needed or monthly.

d. Reporting Limit Standard- Prepared 1.0 ml of RL Stock solution A and 1.0 ml of RL Stock Solution B diluted to 100 ml with 2% HNO3 and 5% HCL matrix , mix well. Solution stable for 3 months

6. Digestion standards

a. The Laboratory control sample (LCS) is prepared from High Purity solutions CLP-CAL-1 solution A and B; CLP-CAL-2 and CLP-CAL-3. 0.50 mL of CLP-CAL-1 A and B is diluted to 500 mL with 0.125 mL of CLP-CAL-2 and CLP-CAL-3. 25 mL of HCl and 10 mL of HNO3 are added for preservation. This solution is stored in a Teflon bottle. A portion is reserved in case of a problem with digestion. When there is a problem with the analysis of the LCS the solution is checked first before action is taken to make sure that it was made properly and has not deteriorated since it was made up. This solution is given a unique identifier. The LCS is prepared from a source independent from that used in the calibration standards. This solution is prepared daily or as needed. Note: The analysis of Molybdenum is not a routine procedure but a project-specific requirement. A customized LCSW mix must be prepared to contain this target analyte.

b. The solid Laboratory Control Sample (Soil) (LCSS) is prepared by weighing up 1.0 g of teflon chips and spiking using the same spiking solutions used to spike the sample matrix. This standard is given a unique identifier i.e. LCSS(date prepared)A,B,C etc.

c. The spiking solutions are prepared as follows:

1. Stock Multi-element Spiking Solutions: High Purity <u>CLP-CAL-1</u> <u>solution A</u>: 2000 ug/mL Al and Ba; 50 ug/mL Be; 200 ug/mL Cr; 500 ug/mL Co, Mn, Ni, V and Zn; 250 ug/mL Cu; 1000 ug/mL Fe; 5000 ug/mL Ca, Mg, K and Na; <u>solution B</u>: 250 ug/mL Ag; <u>CLP-CAL-2</u>: 1000 ug/L Sb; <u>CLP-CAL-3</u>: 1000 ug/mL As, Pb, Se, Tl; 500 ug/mL Cd. Order from the manufacturer already prepared. These solutions are given a unique identifier. Add 0.050 mL (0.20 mL for soil samples) of CLP-CAL-1 solutions A and B, and 0.0125 mL (0.05 mL for soil samples) of CLP-CAL-2 and 3 to 50 mL of sample (1gram of sample for soils) for the following spike values: 2000 ug/L Al and Ba; 50 ug/L Be; 200 ug/L Cr; 500 ug/L Co, Mn, Ni, V and Zn; 250 ug/L Cu; 1000 ug/L Fe; 5.0 mg/L Ca, Mg, K and Na, 250 ug/L Ag, Sb, As, Pb, Se and Tl; 125 ug/L Cd. A blank spike should be prepared at the time the samples are spiked to check the actual spike value and accuracy.

2. TCLP Spiking Solution: Use 0.50 mL diluted to 50 mL for digestion:
2.5 mL 10000 mg/L Ba stock standard diluted to 100 mL; 2.5 mL Cr, Pb and As 1000 mg/L stock standard diluted to 100 mL; 0.50 mL Cd and Se diluted to 100 mL . Store in a Teflon bottle. A blank spike should always be prepared at the same time a sample is being spiked. This solution should produce a spike value of 2500 ug/L Ba; 250 ug/L Cr, Pb and As; and 50 ug/L of Cd and Se. Note: Since the samples are diluted 10x when digested the spike value will appear to be 10x greater when analyzed.

3. TCLP Silver Spiking Solution: Use 5.0 mL diluted to 50 mL for digestion:
0.40 mL of 1000 mg/L stock Ag solution diluted to 200 mL. Store in a Teflon bottle. A blank spike should always be prepared at the same time a sample is being spiked. This solution should produce a spike value of 200 ug/L. . Note: Since the samples are diluted 10x when digested the spike value will appear to be 10x greater when analyzed. Also this solution is not very stable and may require fresh preparation at least weekly.

VIII. CALIBRATION AND ASSOCIATED QA/QC

A. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

B. Operating conditions - **The instrument settings can be found in method file.** For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

C. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions. **(See SOP-106, *ICP Instrument Operation*)** Flush the system with 2% HNO_3 / 5% HCl between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve consists of a blank and three standards ($r \geq 0.995$). If a three point

calibration curve is not required for the client samples being analyzed Empirical Laboratories may use a blank and one standard as referenced in USEPA - CLP protocols.

D. Before beginning the sample run, analyze the Iron and Aluminum standards at their linear range to check for IEC drifts. Analyze these standards first as QC samples with an IEC check table and action taken should be to calculate IECs. Then reanalyze the standard as a sample to check to see if the correction was made successfully. If the IEC correction overcompensated or under compensated for any one metal which is affected by it, the standard should be run again as a QC as before. Make sure to rinse thoroughly after running these linear range standards, they can cause carry over into the initial QC samples which are analyzed next. The analysis order follows as: ICV (± 10%) for 200.7 (± 5%) and ICB (< ±MDL or ±RL/CRDL for others or CLP, **for CCB, DOD QSM Ver. 3 no analytes detected >2xMDL**) first, then reanalyze the highest mixed calibration standard(s) as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5%. If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

E. For CLP projects,verify the validity of the curve in the region of 2x the contract required detection limit (CRDL) before and after each batch of 20 samples in the specific order of CRI, ICSA, ICSAB, CCV and CCB(CCB criteria: < ±MDL or ±RL/CRDL for others or CLP, **for CCB, DOD QSM Ver. 3 no analytes detected >2xMDL, beginning and end of sequence and after every 10 samples**) or twice during every 8-hour work shift, whichever is more frequent. Results should be within ±20%. Supervisor must be notified if the control limit is not met. Supervisor will dictate corrective action if required. The final analytical report must document this situation. (For Internal QC)

F. Verify the interelement and background correction factors at the beginning and after each batch of 20 samples in the specific order of CRI, ICSA, ICSAB, CCV and CCB(CCB criteria: < ±MDL or ±RL/CRDL for others or CLP, **for CCB, DOD QSM Ver. 3 no analytes detected >2xMDL, beginning and end of sequence and after every 10 samples**) or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check solution A and AB. Results should be within ±20% of the true value for ICSAB. **For ICSA DOD QSM Ver 3. , absolute value of concentration for all non-spiked analytes < 2xMDL**.(ICSAB required at the end for CLP projects)

G. *When analyzing samples associated with North Carolina or with DOD QSM Ver. 3 work, a solution containing analytes at their reporting limit must be analyzed prior to sample analysis. The concentrations must be within 20% DOD(20 or 30% depending on project) of their true values to be acceptable.*

Note: Supervisor must be notified if the control limit is not met. Supervisor will dictate corrective action if required. The final analytical report must document this situation.

H. The instrument must be calibrated once every 24 hours if performing straight CLP work.

I. Note: The instrument software is set up to go to the "L" rack for calibration standards, initial IEC standards and initial and continuing calibration verifications (ICV/CCV). This QC is inserted by the analyst when setting up the autosampler table which is what the instrument software uses for a RUN LOG (The software does not allow the analyst to print the actual run log but prints an autosampler report). The autosampler report is used to load the instrument and does not include ICV and CCVs in racks 2 through 5 because all calibration QC is loaded in the "L" rack and then samples and CCB's are loaded in Racks 2 through 5. When the samples are analyzed the software inserts ICVs and CCVs from the actual run log set up by the analyst. Since each CCV location is visited twice by the autosampler during the run, two locations will be called CCV1 and two locations will be CCV2 and so on. The time and date are printed on the instrument print out with the data so that the data user can distinguish between the two CCVs.

J. Instrument Autosampler Report example:

Calibration or "L" Rack(used by instrument software to insert QC)

1) STD 1-blank
2) NAK-100ppm
3) NAK-high
4) Fe-500,000ppb
5) Mn-10,000ppb
6) QC 21-high
7) Al IEC-QC(calculate IEC)
8) FE IEC-QC(calculate IEC)
9) ICV
10) CCV1
11) CCV2
12) CCV3

Sample Sequence RACK 1

1) Al IEC-(readback)
2) Fe IEC-(readback)
3) ICB-initial
4) RL-reporting limit standard

5) NAK 100ppm-(readback)

Sample Sequence RACK 1 (cont.')

6) NAK High-(readback)
7) QC 21 High-(readback)
8) Rinse
9) CRI-0
10) ICAS-0
11) ICASB-0
12) Rinse
13) CCB 1A
14) Preparation Blank
15) Laboratory Control Sample
16) Sample 1
17) Sample 2
18) Sample 3
19) Sample 4
20) Sample 5
21) Sample 6
22) Sample 7
23) Sample 8
24) CCB 1B
25) Sample 9
26) Sample 10
27) Sample 11
28) Sample 12
29) Sample 13
30) Sample 14
31) Sample 15
32) Sample 16
33) Sample 17
34) Sample 18
35) CCB2A
36) Sample 19
37) Sample 20
38) Sample serial dilution
39) Sample matrix spike
40) Sample matrix spike duplicate
41) Sample post digestion spike
42) CRI-1
43) ICSA-1
44) ICSAB-1
45) Rinse
46) CCB 2B
47) Preparation Blank
48) Laboratory Control Sample

RACK 2

1) Sample 1
2) Sample 2
Etcetera…

Each rack holds 48 samples and there are 4 racks that are used for samples and CCBs and run QC other then ICV/CCV's.

IX. PROCEDURE

A. Once the instrument has been calibrated, begin the analysis of samples.

B. If particulates are visible in the digestate, the sample must be filtered prior to analysis. If filtration is required, a filter blank must be prepared by filtering reagent grade water which has been properly acidified. **In the event USACE samples are filtered, all USACE samples and the QC samples in that QC batch must be filtered. All USACE solid samples and their associated batch QC samples must be filtered prior to analysis.**

C. Flush the system with 2% HNO_3 / 5% HCl for at least 1 minute before the analysis of each sample.

D. Dilute and reanalyze samples that are more concentrated than the linear calibration limit or, for 200.7, ± 10% of the linear range standard. **In the case of USACE samples, the criterion changes and requires dilution and reanalysis of all samples which produce a concentration that exceeds the highest calibration standard. Sample results detected between the MDL and RL are flagged as estimated with a "B" flag.**

E. Verify calibration every 10 samples or every 2 hours, whichever is more frequent and at the end of the analytical run, using a continuing calibration verification (CCV) sample and a continuing calibration blank (CCB) sample.

- The results of the CCV are to agree within 10% for 6010 (5% for 200.7) on initial verification of the expected value, with relative standard deviation (RSD) < 5% from replicate (minimum of two integrations). If not, terminate the analysis, correct the problem, and reanalyze the previous ten samples. The analyst may continue the analytical run, and after conferring with the section manager it may be necessary to reanalyze a group of samples. The analyst must notify the section manager within 24 hours.

- The results of the calibration blank (this is not the method/preparation blank) are to agree within < ±MDL(SW-846 Method 6010B), and 3 x IDL or CRDL for CLP, for **DOD QSM Ver. 3 no analytes detected**

>2xMDL. If the calibration blank is not in control, evaluate the impact upon the previous 10 samples. Reanalysis may be required after an evaluation of the data. If the blank < 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, samples need not be reanalyzed. One must also evaluate the reporting limit (RL) as it relates to 3X the IDL/MDL. If the RL is significantly above 3X IDL or MDL then reanalysis may not be required (Na, K, Mg and Ca are good examples of this situation).

- Total hardness is reported from HNO_3 preserved sample. The final concentration is calculated from the calcium and magnesium results as follows:

  Ca mg/L x 2.5 + Mg mg/L x 4.1 = total Hardness in mg/L as $CaCO_3$

F. Documentation of Capability (DOC) – Each analyst must perform a DOC to demonstrate proficiency with this method. Refer to SOP-413 for guidance.

X. CALCULATIONS

A. The instrument will generate data results in mg/L or µg/L (labeled appropriately). Each result represents an average of three individual readings per metal channel.

B. For aqueous samples, if a post/predigestion dilution is performed , the result must be multiplied by this factor or the dilution factor must be entered into the instrument data table in which case the instrument will generate data corrected for the dilution.

C. For solid samples, if a postdigestion dilution is performed , the result must be multiplied by this factor or the dilution factor must be entered into the instrument data table in which case the instrument will generate data corrected for the dilution. Also, the result must be converted to reporting units which are usually mg/kg.

SR (ug/g or mg/kg) = IR*DF*FED/SM

SR = Sample result
IR = Instrument result (µg/L)
DF = Dilution factor (post digestion)
FED = Final volume of digestate (L)
SM = Sample mass digested(g)

XI. QUALITY CONTROL

A. Daily

1. See sections VIII and IX above.

B. Quarterly

1. Linear range standards must be analyzed at a frequency no less than once every three months. The linear range standard represents the second standard required for verification that samples are actually linear to the degree claimed. The analyst is responsible for completing this task in a timely manner. The linear range standard must be within +/-5% of true value.

2. The interelement correction factors (IEC) should be verified at the time the linear range standards are analyzed.

3. IDL's if CLP work required.

C. Digestion

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

2. Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank, sometimes referred to as the preparation blank is a volume of reagent water acidified with the same amounts of acids as were the standards and samples. These blanks are taken through the same digestion/preparation steps as the sample being tested. The result for the method blank should not indicate contamination greater than ± ½ RL (USACE) or ±RL/CRDL for other or CLP. If exceeded, the impact upon the data should be evaluated and the associated sample(s) should be either redigested or the data should be qualified.

3. Employ a minimum of one laboratory control sample (LCS) for aqueous samples or one teflon chip spiked sample per sample batch to verify the digestion procedure. These LCSs are taken through the same digestion/preparation steps as the sample being tested. The control limits are ±15% method 200.7 - aqueous and soil samples or ±20% for all other methods aqueous and soil samples. If the LCS is not in control, the impact upon the client data should be evaluated and the associated sample(s) should be redigested. Consult your supervisor for further action. Qualifying the associated data may not be permissable for CLH.

D. Sample

1. Analyze one replicate sample for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. It is acceptable to substitute a matrix spike duplicate for the sample

replicate. Project specific requirements will take precedence in these situations. NJDEP demands that this requirement be met with a client specific duplicate rather than a spike duplicate. The control limits are 20% RPD (if both are >5x CRDL) or ± the CRDL (if either are <5X CRDL).

2. Analyze one spiked sample and spiked sample duplicate for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. Project specific requirements will take precedence in these situations. If the analyte level in the sample is not greater than 4X the spiking level, the spike recoveries should be within ±25% of the true value. If not, a post digestion spike should be analyzed.

3. The relative percent difference (RPD) between replicate determinations is to be calculated as referenced in the laboratory QA manual. (A control limit of ± 20% RPD (non-aqueous samples may routinely exceed this amount) shall be used for sample values greater than five times the contract required detection limit.) Supervisor must be notified if the control limit is not met. Supervisor will dictate corrective action if required. The final analytical report must document this situation.

4. *The following should be analyzed with each preparation batch containing a matrix spike.*

   - Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 50 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution (volumetric glassware must be used) should agree within ±10% of the original determination. If not, a chemical or physical interference effect should be suspected. The analyst and or section manager must note this situation on the final analytical report.

   - Post digestion spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 85% to 115% of the known value and is required if the pre-digestion matrix spike (low-level only for CLH) is outside of control limits. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The analyst and or section manager must note this situation on the final analytical report.

E. Method Detection Limit (MDL), Empirical Laboratories Reporting Limit (ERL), Contract Required Quantitation Limit (CRQL) and Analyte Wavelength:

TABLE I

Aqueous and Soil Method Detection Limits(MDL), Empirical Laboratories Reporting Limits(ERL), CLP OLM04.1 & OLM05.2 Contract Required Quantitation Limits (CRQL)

Analytes by EPA 200.7,3005A/3050A- 6010B SOW 4.1 & 5.2	AQUEOUS MDL (ug/L)	AQUEOUS ERL (ug/L)	AQUEOUS CRQL ILMO 4.1 (ug/L)	AQUEOUS CRQL ILMO 5.2 (ug/L)	SOLID/SOIL MDL (mg/Kg)	SOLID/SOIL ERL (mg/Kg)	SOLID/SOIL CRQL ILMO 4.1 (mg/Kg)	SOLID/SOIL CRQL ILMO 5.2 (mg/Kg
Silver	**1.0**	**10**	**10**	**10**	**0.20**	**2.0**	**2**	**2**
Aluminum	**50**	**200**	**200**	**200**	**10**	**40**	**40**	**40**
Arsenic	**3.0**	**10**	**10**	**15**	**0.6**	**2.0**	**2**	**3**
Barium	**5.0**	**200**	**200**	**200**	**1.0**	**40**	**40**	**40**
Beryllium	**1.0**	**5.0**	**5**	**5**	**0.20**	**1.0**	**1**	**1**
Calcium	**200**	**5000**	**5000**	**5000**	**20**	**1000**	**1000**	**1000**
Cadmium	**1.0**	**5.0**	**5**	**5**	**0.20**	**1.0**	**1**	**1**
Cobalt	**5.0**	**50**	**50**	**50**	**1.0**	**10**	**10**	**10**
Chromium	**2.0**	**10**	**10**	**10**	**0.40**	**2.0**	**2**	**2**
Copper	**4.0**	**25**	**25**	**25**	**0.40**	**5.0**	**5**	**5**
Iron	**30**	**100**	**100**	**100**	**1.0**	**20**	**20**	**20**
Potassium	**200**	**5000**	**5000**	**5000**	**40**	**1000**	**1000**	**1000**
Magnesium	**200**	**5000**	**5000**	**5000**	**40**	**1000**	**1000**	**1000**
Manganese	**1.0**	**15**	**15**	**15**	**0.20**	**3.0**	**3**	**3**
Sodium	**200**	**5000**	**5000**	**5000**	**40**	**1000**	**1000**	**1000**
Nickel	**3.0**	**40**	**40**	**40**	**1.0**	**8.0**	**8**	**8**
Lead	**1.5**	**3.0**	**3**	**10**	**0.60**	**0.60**	**0.6**	**2**
Selenium	**3.0**	**5.0**	**5**	**35**	**0.60**	**1.0**	**1**	**7**
Antimony	**5.0**	**60**	**60**	**60**	**1.0**	**12**	**12**	**12**
Thallium	**3.0**	**10**	**10**	**25**	**0.60**	**2.0**	**2**	**5**
Vanadium	**5.0**	**50**	**50**	**50**	**1.0**	**10**	**10**	**10**
Zinc	**5.0**	**20**	**20**	**60**	**1.0**	**4.0**	**4**	**12**

TABLE 2

METAL	WAVELENGTH
Aluminum	**308.2**
Antimony	**206.8**
Arsenic	**189.0**
Barium	**493.4**
Beryllium	**313.0**
Cadmium	**226.5**
Calcium	**317.9**
Chromium	**267.7**
Cobalt	**228.6**
Copper	**324.7**
Iron	**271.4**
Lead	**220.3**
Magnesium	**279.0**
Manganese	**257.6**
Nickel	**231.6**
Potassium	**766.4**
Selenium	**196.0**
Silver	**328.0**
Sodium	**330.2**
Thallium	**190.8**
Vanadium	**292.4**
Zinc	**206.2**

XII. CORRECTIVE ACTIONS

A. INSTRUMENT RELATED

1. ICV not within ± 10% or ± 5% for 200.7
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate through analysis of appropriate standards and recheck ICV.

2. ICB not ±MDL or within ± 3X IDL or CRDL for CLP, **DOD QSM Ver. 3 no analytes detected >2xMDL**

a. Is the problem with the solution?
   i. Reprepare
b. Is the problem with the calibration?
   i. Recalibrate with the blank solution or the low level standard. Restart analysis with the ICV.

3. Check standards not within ± 5%
   a. Is the problem with the solution?
      i. Repour, reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.

4. CRI not within ± 20% (Internal QC, only required for CLP work).
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.
5. ICSA metals not present are not less than the CRDL for that metal, **for ICSA DOD QSM Ver 3. , absolute value of concentration for all non-spiked analytes < 2xMDL.**
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.

6. ICSAB not within ± 20%
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.

7. CCV not within ± 10%
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. If appropriate, continue the analysis. Discuss effect of the out of control situation with your supervisor. The samples will be reanalyzed or the data will be qualified. Note: CLH data must always be reanalyzed back to the last compliant CCV and not qualified.

8. CCB not ±MDL or within ± 3X IDL or CRDL for CLP, **DOD QSM Ver. 3 no analytes detected >2xMDL**

a. Is the problem with the solution?
   i. Reprepare
b. Is the problem with the calibration?
   i. Apply SW846 guidance. (See Section IX-E for additional guidance). Note: CLH data must always be reanalyzed back to the last compliant CCB and not qualified.

B. DIGESTION RELATED

1. Preparation blank not within ± ½ RL and ± RL for common contaminants USACE or RL/CRDL for other or CLP
   a. Is the problem with the instrument?
      i. Evaluate with respect to instrumental bias or reanalyze when instrument is in control.
   b. Is the problem with the digestion?
      i. If associated samples are less than 10X the level of the preparation blank but above the RL, the sample must be redigested or the data must be qualified on the final report.

2. LCS not within control limits
   a. Is the problem with the instrument?
      i. Evaluate with respect to instrumental bias or reanalyze when instrument is in control.
   b. Is the problem with the digestion?
      i. If biased low, associated samples must be redigested.
      ii. If biased high, the impact upon the data user must be evaluated. The samples will be redigested or the data will be qualified on the final report.

C. SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20% (if both are >5X CRDL) or ± the CRDL (if either are <5X CRDL).
   a. The associated sample data must be qualified on the final report.

2. Spike analysis recovery not within ±20%
   a. Is the analyte level in the sample greater than 4X the spiking level?
      i. If yes, the spike recovery is not evaluated.
      ii. If no, a post digestion spike must be analyzed and the associated sample data must be qualified on the final report.

3. When required, post digestion spike analysis recovery not within ±15%.
   a. The associated sample data must be qualified on the final report.
   b. For USACE analysis by MSA is required.

4. Serial dilution analysis percent difference not within ±10%
   a. Is the analyte concentration a factor of 50 above the instrumental detection limit after dilution?
      i. If no, the serial dilution data can not be evaluated.
      iii. If yes, a chemical or physical interference effect should be suspected. The analyst and or section manager must note this situation on the final analytical report.

XIII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405 fot instruction of proper disposal of waste generated from this area.

Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIV. REFERENCES

1. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846; Third Edition (Update III)*; Method 6010B

2. USEPA *Code of Federal Requlations, 40, CH 1,PT 136;* Method 200.7; APX-B

3. USEPA *Contract Laboratory Program(CLP) for Inorganics ILM04.1; ILM05.2*

Refer to SOP-431 for common environmental laboratory definitions.

Addendum for USEPA CLPILM 05.2

1. The control limit for the ICSA is at 20% or ±CRQL whichever is greater.
2. Preparation codes are required in the digestion log See SOW Exhibit B for a listing of these codes with definitions.

3. The CRQL check standard is run at the concentration of the respective CRQLs. For a listing of CRQL for this SOW see Exhibit C. Several of the metals concentration levels have changed.
4. The spiking level for CLP ILM 05.2 is at 50 ug/L for selenium. All other spike levels remain the same as in SOW ILM 04.1.
5. The CCV shall be analyzed at a different concentration then the ICV (at or near one-half of the calibration standard concentration.
6. The post digestion spike must be analyzed at 2x the indigenous level of the sample or two times the CRQL whichever is greater.
7. A Non-prepared MDL study must be analyzed and the results of this study used for MDL reporting when sample volumes are not digested.

CHANGES TO FORMS for SOWCLPILM 05.2

1. Forms must be double-sided
2. A photocopy of the instrument's direct sequential readout shall be included.
3. Undiluted samples must be reported as well as diluted samples.
4. J flags are used in place of B flags when a sample has a concentration less the CRQL but greater then or equal to the MDL.
5. A D flag is used for samples reported from a dilution.
6. All results are reported down to the MDL not the IDL.
7. Preparation codes are used on form 13.

   The form for method of standard additions (MSA) has been removed and all subsequent QC has move up one form number in other words form 8 is now serial dilution when it used to be the MSA form,etcetera.

ANALYST DATA REVIEW CHECKLIST Sample Number(s):
Batch Number(s):
Method: 6010B (ICP)

QA/QC Item	Yes	No	NA	Second Level Review
1. Were samples analyzed within USACE holding times?				
2. Was initial calibration curve QC criteria met?				
3. Was all continuing calibration criteria in control?				
4. Did any sample exceed the highest calibration standard? (If yes, were appropriate dilutions made to generate samples concentration within calibration range?)				
5. Did LCS or blank spike meet control limits?				
6. Did MS/MSD meet control limits?				
7. Was the preparation (Method) Blank below the project required detection limits?				
8. Did you return samples back to cold storage immediately after use?				
9. Was hot plate temperature monitored/documented and did you apply the thermometer correction factor?				
10. Sample preparation information is correct and complete.				
11. Analytical results are correct and complete.				
12. The appropriate SOP's have been used and followed.				
14. "Raw data" including all manual integration's have been correctly interpreted.				
15. "Special" sample preparation and analytical requirements have been met.				
16. Documentation complete (e.g., all anomalies in the analytical sequence have been documented, corrective action forms are complete.				

Comments on any "No" response:

_____

_____

_____

_____

_____

_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

FLASHPOINT/IGNITABILITY

METHOD

SW846 – 1010

SOP NUMBER: **SOP-149**

REVISION NUMBER: **1**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

2/25/02

EFFECTIVE DATE

02/08/08

DATE OF LAST REVIEW

FLASHPOINT/IGNITABILITY
SW846 Method 1010

I. SCOPE AND APPLICATION:

A. The Pensky-Marten closed cup tester is used to determine the Flashpoint of liquids.

II. METHOD SUMMARY:

A. The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ingintes the vapor above the sample. Sample results are corrected for ambient barometric pressure after determination.

III. SAMPLING HANDLING AND PRESERVATION:

A. Store samples at 4 ^{o}C. Some samples may require freezing before the test can be accurately measured.

IV. INTERFERENCES:

A. None.

V. EQUIPMENT/APPARATUS:

A. Pensky-Marten closed cup tester with stirring mechanism.

B. Propane.

C. Thermometer capable of reading in 0.5 ^{o}C from -5 to 110 ^{o}C. ASTM 9 C.
Thermometer capable of reading in 2.0° C from 90 to 370° C. ASTM 10 C.

D. Igniter.

VI. REAGENTS:

A. p-Xylene, neat liquid.

VII. PROCEDURE:

A. Fill the test cup with sample up to the line engraved on the inside of the cup.
B. Place the cup in the heater.
C. Heat the sample at a slow, constant rate.

D. Test for a flash by placing the ignition source into the vapor above the sample.
E. Continue to test for a flash every 2 ^{o}C until either the sample flashes or the temperature of the sample reaches 100 ^{o}C.

VIII. CALCULATIONS:

The barometric pressure is read on a digital barometer which measures in inches mercury. Remember to convert to millimeters mercury using the following constant:

1 inch Hg = 25.4 mm Hg

Observe and record the ambient barometric pressure at the time of the test. When the pressure differs from 101.3 kPa (760 mm Hg), correct the flash point as follows:

Corrected flash point = C + 0.033 (769 - P)

Where:

C = observed flash point, °C,
P = ambient barometric pressure, mm Hg

Note: Aneroid barometers, such as those used at weather stations and airports , are precorrected to give sea level readings and would not give the correct reading for this test

IX. QUALITY CONTROL:

A. The Flashpoint of the p-xylene should be determined at the beginning and end of each set of 20 or less samples. The p-xylene should flash at 27 ^{o}C with control limits of +/-2.2 ^{o}C.

REACTIVE SULFIDE

METHOD SW846 CHAPTER 7

SECTION 7.3.4(MODIFIED PER USEPA REGION IV)

SOP NUMBER: **SOP-156**

REVISION NUMBER: **4**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: **06/25/08**

DATE OF LAST REVIEW: **06/25/08**

REACTIVE SULFIDE

REFERENCE:
SW846 CHAPTER 7, SECTION 7.3.4(MODIFIED PER USEPA REGION IV)

I. SCOPE AND APPLICATION

A. This method is applicable to all wastes, with the condition that wastes that are combined with acids do not form explosive mixtures.

B. The method provides a way to determine the specific rate of release of hydrogen sulfide upon contact with an aqueous acid.

C. This procedure releases only the hydrogen sulfide evolved at the test conditions. It is not intended to measure forms of sulfide other than those that are generated under the test conditions.

II. SUMMARY OF METHOD

An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The sulfide is oxidized to sulfur by adding a known excess amount of iodine. The excess iodine is determined by titration with a standard solution of sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantitation is based on the sodium thiosulfate.

III. SAMPLE COLLECTION, HANDLING AND PRESERVATION

A. Samples containing, or suspected of containing, sulfide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Samples should be kept under refrigerated storage until analysis begins.

B. It is suggested that samples of sulfide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base and adding zinc acetate to the sample, this will cause dilution of the sample, increase the ionic strength, and, possibly, change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrogen sulfide.

C. Testing should be performed in a ventilated hood.

D. Keeping consistency with the holding times established for the TCLP procedure (which is also part of the Hazardous Waste Characterization Suite), the recommended holding time for the distillation of reactive sulfide is 14 days from the time of collection. The sample must be distilled and analyzed within 14 days from sampling.

IV. INTERFERENCES

Interferences are undetermined. They will vary with the type of wastes and their intrinsic contamination levels.

V. APPARATUS AND MATERIALS

A. Round-bottom flask - 500 mL, three-neck, with 24/40 ground-glass joints.

B. Gas scrubber - 50 mL calibrated scrubber.

C. Stirring apparatus - To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination, or an overhead motor-driven propeller stirrer.

D. Addition funnel - With pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve.

E. Flexible tubing - For connection from vacuum/cooling supply to apparatus.

F. Vacuum and cooling system.

G. Analytical balance - Capable of weighing to 0.001 g.

H. 500 mL flasks.

I. Hot plate stirrer.

J. 25 mL buret.

K. Volumetric pipets.

VI. REAGENTS

A. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

B. Reagent water. All references to water in this method refer to reagent water, as generated in the laboratory through a deionization/purification system.

C. Sulfuric acid (10% per USEPA Region IV), H_2SO_4. Add 100 mL concentrated H2SO4 to 900 mL of Reagent water. Cool to room temperature.

D. Sulfide reference solution. Dissolve 4.02 g of $Na_2S \cdot 9H_2O$ in 1.0 liter of reagent water. This solution contains 570 mg/L hydrogen sulfide. Dilute this stock solution to cover the analytical range required (100 to 570 mg/L). **(Purchased commercially)**

E. Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in reagent water and dilute to 1 liter with reagent water.

F. Sodium hydroxide solution (0.25N), NaOH. Dilute 200 mL of 1.25N sodium hydroxide solution (Step E) to 1 liter with reagent water.

G. Sodium Hydroxide, 6N: dissolve 240 grams of NaOH in about 600 mL of reagent water. Dilute to 1 liter.

H. Hydrochloric acid, 6N: add 250 mL concentrated HCl to 250 mL reagent water, mix well.

I. Standard iodine solution, 0.025N: dissolve 20 to 25 grams KI in a little water and add 3.2 grams iodine. After iodine has dissolved, dilute to 1000 mL in a volumetric flask. Standardize against 0.0250N Na_2S0_3, using thyodene as indicator. **(Purchased commercially)**

K. Standard sodium thiosulfate titrant solution, 0.025N: dissolve 6.205 grams $Na_2S_20_3 \cdot 5H_20$ in distilled water. Add 1.5 mL 6N NaOH or 0.4 grams solid NaOH and dilute to 1000 mL. Standardize with bi-iodate solution. Or purchase commercially.

L. Standard potassium bi-iodate solution, 0.0250 N: dissolve 812.4 mg KH(IO3)2 in distilled water and dilute to 1000 mL. Standardization of thiosulfate--dissolve approximately 2 grams KI, free from iodate, in an Erlenmeyer flask with 100 to 150 mL distilled water. Add 1 mL 6N H_2SO_4 or a few drops of concentrated H_2SO_4 and 20.00 mL standard bi-iodate solution. Dilute to 200 mL and titrate liberated iodine with thiosulfate titrant, adding 1 scoop thyodene toward end of titration, when a pale straw color is reached. When the solutions are of equal strength, 20.00 mL 0.0250 N $Na_2S_2O_2$ should be required. If not, adjust the $Na_2S_20_3$ solution to 0.0250 N using N1V1 = N2V2 equation.

M. Thyodene.

VII. PROCEDURE

A. Add 50 mL of 1.25N NaOH solution to a calibrated scrubber and dilute with reagent water to obtain an adequate depth of liquid.

B. Assemble the system, so that the nitrogen is coming in through a pasteur pipette under the surface of the waste where it will bubble through the waste as the acid is added. Turn on the Nitrogen and make sure there is an adequate flow.

C. Add 10 g of the waste to be tested to the system and make sure that the system is air tight.

D. With the nitrogen flowing, add enough of the 10% H2S04 to bring the pH of the waste down to 2.0, while starting the 30-minute test period. This will take some experimentation with an aliquot of the waste before distillation to determine how much acid to add.

E. Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test. The vacuum should be generating 2-3 bubbles per second through the liquid.

Note: The stirring should not be fast enough to create a vortex.

F. After 30 minutes, turn off the nitrogen and disconnect the scrubber. Dilute the scrubbing solution to 250 mLs in a volumetric flask using reagent water.

G. Determine the pH of the waste left in the flask to make sure that a pH of 2 has been reached.

H. Pipet a known amount of standardized 0.025N iodine solution (VI.J) in a 500-mL flask, adding an amount in excess of that needed to oxidize the sulfide.

I. Pipet 12 mLs of 6M HCl into the iodine in the 500 mL flask. (note: this volume of acid is what it normally takes to take 200 mLs of the 1.25N NaOH scrubber solution to a pH of 2.

J. Pipet 200 mLs of the gas scrubbing solution obtained in Step F to the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Step H for calculations. Record the total volume of standardized 0.025N iodine solution used.

L. Titrate the solution in the flask with standard 0.025N sodium thiosulfate solution. Titrate slowly with sodium thiosulfate titrant adding 1 scoop thyodene reagent toward the end of the titration, when a pale straw color is reached. The sample will go from straw yellow to a dark blue when thyodene is added. It should take only 2 or 3 drops of titrant to bring sample to the endpoint of clear at this point. Record mL of titrant used. Sample will turn back blue but the first change from blue to clear is the endpoint.

N. Calculate the concentration of sulfide using the following equation:

$$\frac{(\text{mL Iodine} \times \text{N Iodine}) - (\text{mL titrant} \times \text{N titrant}) \times \left(\frac{32.06\ \text{g}}{2\ \text{eq.}}\right)}{\text{sample volume (L)}} = \text{sulfide (mg/L)}$$

VIII. CALCULATIONS

Determine the specific rate of release of H_2S, using the following parameters:

X = Concentration of H_2S in scrubber (mg/L)
(This is obtained from VII.N)

L = Volume of solution in scrubber (L)

W = Weight of waste used (kg)

S = Time of experiment (sec) = Time vacuum stopped - Time vacuum started

R = Specific rate of release (mg/kg/sec) = $\frac{X \cdot L}{W \cdot S}$

Total releasable H_2S (mg/kg) = R x S

IX. METHOD PERFORMANCE

The operation of the system can be checked and verified using the sulfide reference solution (Step VI.D). Perform the procedure using the reference solution as a sample and determine the percent recovery. Evaluate the standard recovery based on historical laboratory data.

X. QUALITY CONTROL

A. With each batch, or every 20 samples, a method blank must be analyzed.

B. The nature of the waste sample may interfere with the efficiency of a direct spike on the original matrix. Depending on the project requirements or the data quality objectives, addition of the spike amount to the distillate may be acceptable. An MS/MSD set is recommended every 20 samples.

XI. CORRECTIVE ACTION

A. If any problems occur, discuss the appropriate corrective action with the Section Manager.

B. If the volume of 1.25 N NaOH and reagent water is too low in the NaOH scrubbers, low recoveries will usually occur. The addition of some reagent water to the NaOH scrubber will correct this problem.

XII. HEALTH AND SAFETY

A. Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of gloves and lab coats is highly recommended.

B. Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples which need special consideration have applicable notes on the sample logs.

A. MSDS sheets are available for all reagents and standards which have been purchased. These are located on the bookshelf outside the office supply storage room.

XIII. POLLUTION PREVENTION

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

B. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

C. For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

XIV. WASTE MANAGEMENT

A. The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be

characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel," available from the American Chemical Society at the address listed in Section 14.3 from method 300.1.

DISTILLATION OF AQUEOUS/SOLID SAMPLES FOR TOTAL AND NON-AMENABLE CYANIDE ANALYSIS

METHODS 335.1/335.4/Standard Methods SM4500-CN C,G, 18th, 19th ED./ (SW846) 9012A/USEPA CLP ILMO 4.1
(NJDEP does not accept CLPILM 04.1 after June, 2003)
Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

SOP NUMBER: SOP-164

REVISION NUMBER: 12

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 11/29/06

DATE OF LAST REVIEW: 01/09/08

DISTILLATION OF CYANIDE, TOTAL AND AMENABLE

REFERENCE:
SW846 METHOD 9012A, USEPA Methods 335.1, 335.4, Standard Methods SM 4500-CN C,G, 18th, 19th ED. / CLP ILMO 4.1
See Addendum for USEPA CLPILM 05.2 (Aqueous, Soil/Sediment)

I. SCOPE AND APPLICATION

A. This method is applicable to the distillation of cyanide from drinking, surface, and saline waters, domestic and industrial wastes, and soil/sediments.

B. The limit of detection for waters is 0.0050 mg/L and the limit of quantitation is 0.010 mg/L. The limit of detection for soils is 0.13 mg/kg and the limit of quantitation is 0.25 mg/kg.

II. SUMMARY OF METHOD

A. The cyanide as hydrocyanic acid is released from cyanide complexes by means of a reflux distillation operation, and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

B. Cyanide is defined as cyanide ion (CN^-) and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

III. SAMPLE HANDLING AND PRESERVATION

A. The sample should be collected in plastic or glass bottles of 100 mLs. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.

B. Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.06 g of ascorbic acid for each liter of sample volume.

C. Samples (not including soils/sediments) must be preserved with 2 mL of ten normal sodium hydroxide per liter of sample (pH $\geq$12) at time of collection.

D. Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator to maintain temperature at 4°C.

E. The holding time for cyanide is 14 days counting the day of sampling as the first day. This applies for soils as well as waters. Samples must be distilled and analyzed within 14 days of sampling.

IV. INTERFERENCES

A. Interferences are eliminated or reduced by using the distillation procedure.

B. Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation, must be treated by adding lead acetate, or if the sulfide concentration is too high, add powdered lead carbonate [$Pb(CO_3)_2$] to avoid significantly reducing pH. Repeat test until a drop of treated sample no longer darkens the acidified lead acetate test paper. Filter sample before raising pH for stabilization.

C. High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN.

D. The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser.

V. SAFETY

A. **CAUTION: KCN is highly toxic. Avoid contact with standard solutions.**

B. If an alkaline solution containing simple cyanide is acidified, the simple cyanide will be released.

C. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential heath hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

D. Your laboratory manager and/or Safety Officer is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. A formal safety plan is also available. Use proper personal protection equipment, PPE, such as safety glasses, gloves and laboratory coats should be warn when handling samples and chemicals.

VI. EQUIPMENT/APPARATUS

A. Reflux distillation apparatus such as shown in Figure 1 of the method. Midi distillation apparatus which uses Hammett Scientific Glassware Note: This glassware is made to fit our specific block digester for cyanide. Glassware orders must be made in advance since they are not made until ordered.

VII. REAGENTS AND STANDARDS PREPARATION

A. Reagents

1. **Sodium Hydroxide, 0.25N**: Dissolve 10 g grams of NaOH in DI water and dilute to 1 liter with DI water. Store in a labeled plastic container at room temperature.

2. **Sulfuric Acid 1:1:** Slowly add 500 mL of concentrated H_2SO_4 to 500 mL DI water. Use caution because solution will become extremely hot!! Allow to cool while continuing to stir. Store in a labeled container at room temperature.

4. **Magnesium Chloride Solution**: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1 liter flask; dissolve and dilute to 1 liter with DI water. Store in a labeled plastic container at room temperature.

5. **Chlorine Bleach Made with Sodium Hypochlorite**, such as Chlorox.

6. **Rhodanine Indicator**:
   Dissolve 20 mg of p-dimethyl-amino-bensalrhodanine in 100 mL acetone.

7. **Sulfamic Acid:** Dissolve 40 g of sulfamic acid in DI water, dilute to 100 mL (saturated solution). **NOTE:** When making this reagent for use with the maxi-distillation system the 40 g of sulfamic are diluted to one liter with DI water

8. **Phenolphthalein solution:** Commercially prepared.

9. **Lead Acetate Test Paper**: Commercially prepared.

10. **Acetate Buffer Solution, pH 4.0:** Dissolve 146g anhydrous $NaC_2H_3O_2$, or 243 g $NaC_2H_3O_2.3H_2O$, in 400 mL distilled water, add 480 g conc. acetic acid, and dilute to 1 L with chlorine-demand-free water.

11. **Lead Acetate**

12. **Powdered Lead Carbonate [$Pb(CO_3)_2$]**

B. Standards

1. Traceability

a. A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

b. All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date and the logbook where information is recorded. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

c. The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

2. Preparation

a. Stock Cyanide Solution at 1000 mg/L: Commercially prepared.

b. Working Standard Cyanide Solution: Prepare fresh daily by diluting 1 mL of stock cyanide solution to 100 mL in a volumetric flask with using 0.25N NaOH as diluent. 1 mL - 10 µg CN. Record the preparation in the log book.

c. Performance Evaluation (PE) samples which we have analyzed and received true values for are used for the Laboratory Control Samples. These PE samples are given a unique identifier and all information such as expiration date (typically one year from the date made), source, concentration and preservation are recorded in the Inorganic Standards book A (ISA). The ISA # assigned is used to label this PE sample and is used on all data to trace it back to its source and true concentration.

VIII. CALIBRATION

A. Not applicable. See SOP-175 "**POST DISTILLATION ANALYSIS OF CYANIDE BY THE LACHAT"** for analysis.

IX. PROCEDURE

A. Pretreatment for cyanides amenable to chlorination

1. Two sample aliquots are required to determine cyanides amenable to chlorination. Place one 25 mL aliquot or a volume diluted to 25 mL, in a 100 mL beaker, under the hood, add a stirring bar, and place on a magnetic stirrer, and start stirring bar turning.

2. Check pH and adjust to between 11 and 12 units, with 1.25N NaOH. Use NaOH pellets if solution is highly buffered.

3. Add sodium hypochlorite chlorine bleach (Clorox) solution dropwise until a drop of well-mixed sample turns KI starch paper a distinct blue color. Add about 10 drops excess bleach. (Caution: the initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride.) Maintain this excess for one hour, continuing agitation. Check periodically during the hour (15 minute intervals) to make sure an excess is maintained. If necessary, add additional hypochlorite bleach solution. Also check the pH and adjust back up to 11 to 12 units if necessary.

4. After one hour, add 0.025 g portions of ascorbic acid until KI starch paper shows no residual chlorine. Add an additional 0.025 g of ascorbic acid to ensure the presence of excess reducing agent.

5. Turn off stirring plate and remove stirring bar. Proceed with distillation as in the procedure.

6. Test for total cyanide in both the chlorinated and unchlorinated aliquots. (The difference of total cyanide in the chlorinated and unchlorinated aliquots is the cyanide amenable to chlorination.)

B. Spikes and high and low check standards

1. **Spikes**: Matrix spikes are prepared by diluting 2.5 mL of the High DCV solution in #3 below, to 25 mL with sample (adding 22.5 mL of sample and 2.5 mL of DCV high to the distillation tube). The concentration of this spike is 0.10 mg/L.

2. **Low Distilled Check standard (low DCV).** Dilute 2.0 mL of the 10 mg/L working standard to 100 mLs in a volumetric flask. Then dilute 6.0 mLs of this solution to 25 mLs with 0.25N NaOH, to make a 0.048 mg/L standard.

3. **High Distilled Check standard (high DCV).** Dilute 10 mLs of the 10 mg/L working standard to 100 mLs in a volumetric flask with DI water. Then dilute 5 mLs of this solution to 25 mLs with 0.25N NaOH, to make a 0.20 mg/L standard.

C. Distillation

1. For Waters: Place 25 mL of sample, or an aliquot diluted to 25 mL, in a sample tube. 0.25 N NaOH must be used for all sample dilutions following the distillation.

2. For Soils or Sludges:

   a.) It is extremely important that waste (when appropriate), soil and sediment samples be mixed thoroughly to ensure that the sample is as representative as possible of the sample media. The most common method of mixing is referred to as quartering. The quartering procedure should be performed as follows:

   - The material in the sample pan(inorganic-plastic/organic-aluminum) should be divided into quarters and each quarter should be mixed individually.
   - Two quarters should then be mixed to form halves.

- The two halves should be mixed to form a homogenous matrix.

This procedure should be repeated several times until the sample is adequately mixed.

NOTE: Samples that are clay type materials should be handled in a different manner. Due to these type sample matrices having an affinity to stick to most anything that touches it, another approach must be followed. Obtain a representative sub-sample aliquot from the center or middle section of the sample container.

b.) Accurately weigh a representative 1-g minimum (record actual weight) portion of wet-weight sample (unless there are project-specific requirements where a lower detection limit is required) and transfer it to a sample tube. Add 25 mL of 0.25 N NaOH. Shake or stir the sample so that it is dispersed.

3. Add one drop of Phenolphthalein solution to verify preservation. A positive test is indicated by a bright pink color. If not add a small amount of NaOH.

4. To test for sulfide, place a drop of sample on lead acetate paper, previously moistened with acetic acid buffer solution (pH 4). A positive test is indicated by a black color on the paper.

   a.) If positive the sample will need to be filtered through 934AH filter paper. (4.5cm size) The filtrate will be treated and the filter added back to the treated filtrate before distillation.

   b.) Treat filtrate with powdered lead carbonate [$Pb(CO_3)_2$]. Repeat test until a drop of treated sample no longer darkens the acidified lead acetate test paper.

   c.) Filter the resulting precipitate (should form a lead sulfide which will be black in appearance).

   d.) Once the filtrate is treated and filtered, the filter with the original solids from the pretreated sample will be added back to the treated filtrate and then distilled.

5. Add 25 mL of sodium hydroxide solution 0.25N to the absorber and assemble the apparatus as shown in Fig. 1.

6. Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum such that air bubbles from the thistle tube in the flask at a rate of 3 to 5 per second.

   Note: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It may be necessary to readjust the air rate occasionally to prevent the solution in the sample tube from boiling and spewing out through the thistle tube.

7. Turn on condenser water.

8. Add 0.5 mLs of sulfamic acid through the thistle tube.

9. Slowly add 2 mL 1:1 H_2SO_4 through the thistle tube.

10. Add 2 mL 2.5 M $MgCl_2$ through the thistle and rinse it down with deionized water.

11. Reflux at 100°C for 90 minutes, turn off heat, allow to cool with pump on for 15 minutes.

12. Disconnect absorber and transfer the solution from the absorber into a storage container.

14. Record distillation information in the distillation log. Include date, analyst, sample number, client, matrix, position, sample mass / volume, distillation time, cool down time, when transferred to analyst, when analyzed.

X. CALCULATIONS

A. Sample volumes / masses must be recorded accurately in the distillation log to allow the analyst to correctly calculate the final concentration of cyanide correctly.

XI. DISTILLATION GLASSWARE CLEANING & LABELING

A. The distillation glassware is cleaned thoroughly with hot soapy water between distillations. 1:1 HCl is aerated through the frits on the block to ensure that the frits are clean. Deionized water is forced up through the glassware to rinse it. The cold fingers are dipped in mild acid, rinsed and wiped off.

B. All glassware must be labeled and each position's label must be recorded in the distillation log with the sample that was distilled in that particular vessel.

C. When sample concentrations are at or exceed 1000 mg/L a deionized water blank must be distilled in the exact glassware used for that sample before processing any other client's sample to ensure that the glassware is cleaned and has no residual cyanide to carryover.

XII. QUALITY CONTROL

A. With each distillation batch of samples (maximum of 20 samples) a preparation blank (PB) must be distilled.

B. Each distillation batch of aqueous samples **requires a laboratory control sample (LCS) each day or per 20 samples whichever is more frequent.** Under CLP the LCS serves as the distilled ICV.

C. With each distillation batch of soil samples a soil LCS **each day or per 20 samples whichever is more frequent.**

D. A high and low check standard (DCV/ICV) must be distilled each day or per 20 samples whichever is more frequent. A non-distilled check standard must be prepared daily. This will be used to verify the preparation of the DCV if the DCV results are outside the specification limits. Under CLP the aqueous LCS serves as the ICV.

E. A sample spike (MS) and sample spike duplicate (MSD) are performed with each set of twenty samples. CLP requires 1 duplicate and 1 spike per batch. All QC samples should be taken through the whole procedure including distillation. Spikes are added to the boiling flask in the same manner as standards adding 25 mL of samples or a dilution as used for the unspiked sample. Spike concentration is listed in the method. The addition of the spiking solution must be witnessed and such must be noted in the digestion log.

XIII. CORRECTIVE ACTION

A. If any problems, such as low or high recovery for check standards or LCSs occur, contact the Group Leader. Problems most frequently encountered (for the distillation procedure) are listed below.

B. Recoveries are affected in various ways.

1. If the spiking solution is not prepared properly (e.g., making the proper dilutions), the check standard will be out of control. Caution should be used in calculating the dilution and performing the pipetting.

2. Also, the air flow from the vacuum pumps can cause low recovery. Pay attention to the air flow (it should be in the area of 1 to 2 bubbles per second). If it is too great the HCN does not have an adequate amount of time to be absorbed by the NaOH solution.

3. If the heating block is not heating properly, this will also lead to low recovery. During the distillation, periodically check the sample tubes for the presence of heat (tubes should be very hot to the touch).

4. The addition of all reagents, including the spiking solution, is essential. Without the $MgCl_2$, 1:1 H_2SO_4, or spiking solution, the percent recovery will suffer greatly for complex cyanide. The recovery of simple cyanides will usually be unaffected.

5. If the volume of 0.25 N NaOH and reagent water is not accurate in the NaOH absorber tubes, low recoveries will usually occur.

B. Spike recoveries are affected in similar ways. Refer to the above suggestions. Also, if possible, do not spike a sample that is known to be high in cyanide. This may cause recovery and calculation problems.

XIV. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

The following is a list of changes for sample preparation when the 5.2 statement of work is required:

1. The ICV shall be distilled.

2. Boiling chips are to be added to each sample. Midi-Distillation is reflux 1.5 hours then the heat and vacuum is turned off and the samples cool an additional 15 minutes.

3. The QC criteria for both the Distillation Check QC and the distilled ICV is ±15%.

4. A CRI is required at the beginning and end of each run and for every 20 samples. The QC criteria for the CRI is ±30%.

5. Rounding rule for the appropriate level of precision is that the figure following those to be retained is $\geq$ 5, round up: otherwise round down. (examples: 1.5 and 2.5 would be 2 and 3 respectively rounded up; 1.4 and 2.4 would be 1 and 2 respectively rounded down) Please see Exhibit B, Section 3, (3.3.9.1) of SOW ILM0 5.2 for more guidance on rounding significant figures.

POST-DISTILLATION ANALYSIS FOR CYANIDE BY THE LACHAT METHODS 335.4;(SW846) 9012A USEPA-CLP 4.1 (NJDEP does not accept CLPILM 04.1 after June, 2003) Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

SOP NUMBER: **SOP-175**

REVISION NUMBER: **9**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: **07/18/06**

DATE OF LAST REVISION: **07/0708**

POST DISTILLATION ANALYSIS OF CYANIDE BY THE LACHAT
0.005-0.500 mg CN^-/L

References:
USEPA METHOD 335.4/(SW846) 9012A/USEPA CLP ILMO 4.1
See Addendum for USEPA CLPILM 05.2 (Soil/Sediment)

I. PRINCIPLE

Cyanide from alkaline distillates is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at pH lower than 8. The CNCl then forms a red-blue dye by reacting with pyridine-barbituric acid reagent. The color is read at 570 nm.

II. INTERFERENCES

1. For total cyanide, most interferences are eliminated or minimized by the distillation procedure. Sulfides (sulfides are removed with a lead acetate scrubber using the maxi distillation system) fatty acids, aldehydes and thiocyanates may distill over. See Empirical Laboratories Method SOP-164 for distillation procedure.

III. SPECIAL APPARATUS

1. Lachat Quick Chem AE Automated Ion Analyzer

2. Cyanide manifold (Lachat)

IV SAMPLE HANDLING AND PRESERVATION:

The color reaction is pH sensitive. Therefore, distillates and standards should be carefully matched with respect to NaOH concentration. The distillates are 0.25 N NaOH.

V. SAMPLE PREPARATION

The samples for analysis come directly from the midi-scale distillation procedure.

VI. PREPARATION OF REAGENTS

Use deionized water (<10 megaohm) for all solutions.

Degassing with helium

To prevent bubble formation in the flow cell which can cause inaccurate readings due to airspikes (characterized by poor peak integrity factors (PIF) and/or inaccurate results) degass all solutions except the standards and the Pyridine-Barbituric Acid reagent with helium. Use Helium at 140 kPa (20 lb/in^2) through a helium degassing tube (Lachat part 50100). Bubble Helium vigorously through the solution for one minute.

Reagent 1. Carrier, 0.25 M Sodium Hydroxide

In a 1L vol. flask add 200 mL of 1.25N NaOH (which is used in the SOP-164 distillation method) to approximately 600 mL of D.I. water. Dilute to 1 L, invert to mix. This will ensure that the concentration of the NaOH used for the distillates will be the same concentration used for the carrier solution.

Reagent 2. Phosphate Buffer, 0.71 M

In a 1 L volumetric flask, dissolve 97 g anhydrous potassium dihydrogen phosphate (potassium phosphate, monobasic, anhydrous, KH_2PO_4) in approximately 800 mL water. Dilute to the mark and invert to mix. Prepare fresh monthly.

Reagent 3. Chloramine-T Hydrate

To a 500 mL volumetric flask add about 250 mL water, then add 2.0 g chloramine-T [$CH_3C_6H_4SO_2N(Cl)Na \times H_2O$]. Dilute to the mark and invert to mix. Prepare fresh daily. The shelf life of the chloramine-T can be a critical factor in the Lachat run. New Chloramine-T should be ordered every 6 months. (Analyst discretion should be used).

Reagent 4. Pyridine-Barbituric Acid Reagent

In the fume hood, place 15.0 g barbituric acid in a 1 L beaker and add 100.0 mL water, rinsing down the sides of the beaker to wet the barbituric acid. Add 75 mL pyridine (C_5H_5N) with stirring and mix until the barbituric acid dissolves. Add 15 mL concentrated hydrochloric acid (12 M HCl) and mix. Transfer to a 1 L volumetric flask, dilute to the mark, and invert to mix. This reagent is stable for approximately six months if stored in a cool, dark place.

VII. PREPARATION OF STANDARDS

Traceability

A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date and the logbook where information is recorded. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

Standard 1. 1000 mg CN/L [~1,000 mg CN^-/L (Stock)]

The Stock Standard is purchased from a vendor. **CAUTION: KCN is highly toxic. Avoid contact with standard solutions. Use gloves and protective equipment when handling standards and samples.** This solution is given a unique identifier.

NOTE: The cyanide ion present in the original sample is concentrated by the macro-distillation procedure. The standards preparation recipes below are for standards which are not distilled. These standards are prepared in 0.25 M NaOH to match the matrix of the distilled samples. Since the samples are concentrated by a factor of two; a x 0.50 correction factor must be included in the final manual dilution factor entered into the Lachat. For example, a x 100 dilution would have a final manual dilution factor of 50 and an undiluted sample would have a final manual dilution factor of 0.50.

Record preparation in the appropriate log book.

Standard 2. Working Standard (10.0 mg CN/L)

Pipette 2.00 mL Standard 1 into a 200 mL volumetric flask. Dilute to the mark with Reagent 1, 0.25 M Sodium Hydroxide. Invert to mix.

Set of six calibration Standards:

10 mL of 10 mg/L diluted to 100 mL = 1.0 mg/L std
5.0 mL of 10 mg/L diluted to 100 mL = 0.500 mg/L std
2.0 mL of 10 mg/L std diluted to 100 mL = 0.200 mg/L std
1.0 mL of 10 mg/L std diluted to 100 mL = 0.100 mg/L std
4 mL of 0.500 mg/L std diluted to 100 mL = 0.020 mg/L std
2 mL of 0.500 mg/L std diluted to 100 mL = 0.010 mg/L std
1 mL of 0.500 mg/L std diluted to 100 mL = 0.0050 mg/L std
Blank consists of 0.25 M NaOH
10 mL of 10.0 mg/L std diluted to 200 mL = 0.500 mg/L chk std

The diluent for all standards is 0.25 M NaOH.

NOTE: The cyanide standards are labeled by their actual concentration as determined by standardization of the cyanide stock. For example, if the cyanide stock was determined to have a concentration of 994 mg/L (instead of 1,000 mg/L) then the "1.00 mg/L" std would actually be 0.9940 mg/L, the "0.200 mg/L" std would be 0.1988 mg/L, and so forth. Assigning values to the standards is done under the "Method Definition" option on the Lachat computer.

Record preparation in the appropriate log book.

VIII. INSTRUMENT INFORMATION (see page 12 for manifold diagram)

Analyst should confirm the following:

A. Timing:

Sample throughput: 80 samples/h; 40 s/sample
Pump speed: 35 RPM

Cycle Period: 45 s
Inject to start of peak period: 28 s
Inject to end of peak period: 61 s

B. QuikChem AE Settings:

1) Parameter, Data Window:

Top Scale Response: 0.50 abs
Bottom Scale Response: 0.00 abs

2) Segment/Boundaries

A - 0.50 mg CN/L
F - 0 mg CN/L

3) Results/Approval, Reports

In the default Report definition file (RDF), change:
-Set Default Chord 0 to
-Set Default Chord 3
(Peak should be centered in chord 3)
This change must be made to both the sample and the calibration RDF's.

C. System Notes:

1. Allow enough time for heating unit to warm-up to 60°C with D.I. water pumping through all reagent lines at full speed. (approximately 30 min.)

IX. CALCULATIONS

A. Aqueous Samples:

The Lachat reports the concentration of the final distillate in mg/L. To correct for the X2 concentration by the distillation process, a x 0.50 correction factor must be included in the final manual dilution factor when defining a tray in the Lachat computer. For example, a x 100 dilution would have a final manual dilution factor of 50 and an undiluted sample would have a final manual dilution factor of 0.50. After the application of the X0.5 correction factor, the detection limit is 0.005 mg/L.

B. Solid Samples:

The Lachat reports the concentration of the final distillate in mg/L. Results for solid samples should be in mg/kg and can be obtained by entering the appropriate dilution factor when defining the tray. Conversion from mg/L to mg/kg can be accounted for by the following formula:

$$\left[\frac{\text{mg CN}^-}{\text{Kg sample}}\right]=\left(\frac{\text{N mg}}{\text{1 L soln}}\right)\left(\frac{\text{0.50 L soln}}{\text{g sample}}\right)\left(\frac{\text{1,000 g sample}}{\text{1 Kg sample}}\right)(\text{Wet Weight})$$

From this formula a dilution factor can be obtained. For example if 2 grams of soil were used then this would be a x 250 dilution. When the x 0.50 correction factor is included a final manual dilution factor of x 125 is obtained.

N would be the value obtained from the Lachat without a correction factor. The minimum value for N is 0.01 mg/L soln.

C. Data reporting

1. Reduce data to the result which will be reported.

2. Complete the data review checklist (attached). This must be completed and attached to each set of USACE data.

X. QUALITY CONTROL (Reference SW-846, Update III and USEPA CLP ILMO 4.1 for further clarifications)

A. QA/QC, distilled:

1. PB (preparation blank)

   500 mL of DI water are distilled. When brought up to 250 mL volume following the distillation process a 0.25 M NaOH solution is obtained. A blank is distilled every batch of samples. If the absolute value of the PBW is not below the CRDL or the RL **or ½ the CRDL for Navy Projects** the analyst's supervisor should be consulted before proceeding.

2. DCV (distilled calibration verification)/ICV (distilled/CLP)

   a. The DCV is a check standard generally of a concentration of about 0.200 mg/L. A DCV is put on with every set of distilled samples. There is a maximum of 10 samples in a set. If the DCV is not within ±10 % of the undistilled value the analyst's supervisor should be consulted before proceeding. This sample is given a unique identifier in the distillation log. **USACE projects require both a high and low level DCV and they should compare within ±10% of the undisdilled standards. A corrective action report (CAR) will be required if the limit is exceeded.**

b. CLP requires the ICV to be distilled and from a second source. Must be analyzed immediately after calibration. For water samples the ICV will serve as the LCS (water only). Soils require bath. The control limit is ± 15%.

3. LCSW (laboratory control sample-water)

The laboratory control sample is a second source check on the calibration and must be run once every 20 aqueous samples. The control limits are in-house-generated. The CLP control limits is 80 to 120%. If the LCSW is not within control limits the analyst's supervisor should be consulted before proceeding. This sample is given a unique identifier in the distillation log.

4. LCSS (laboratory control sample-soil)

The LCSS is a second source check with a soil matrix and must be run once every 20 solid phase samples. The control limits are in-house-generated. Under CLP the agency may set the limits. If not, use in-house control limits. If the LCSS is not within control limits the analyst's supervisor should be consulted before proceeding. This sample is given a unique identifier in the distillation log.

5. MS/MSD (matrix spike/matrix spike duplicate)

A spike and spike duplicate (CLP requires 1 duplicate and 1 matrix spike) are done with each batch or 20 samples. The spike concentration will usually be the same as the DCV and spikes are added to the boiling flask in the same manner as check standards. Included in the boiling flask will be the sample aliquot. The total volume for the matrix spike is 500 mL. If the percent recovery for the MS or MSD is not within ±25 percent of the spike concentration, the analyst's supervisor should be consulted before proceeding.

6. Documentation of Capability (DOC) - Each analyst must perform a DOC to demonstrate proficiency with this method. Refer to SOP-413 for guidance.

B. QA/QC, undistilled:

1. ICV (initial calibration verification)

The ICV is an undistilled check standard made from the working standard solution. The concentration is usually around the midpoint of the calibration curve (about 0.500 mg/L). The ICV is analyzed at the beginning of each Lachat run. If the ICV is not within ±10 percent of its true value, the analyst's supervisor should be consulted before proceeding. The calibration verification standard must be prepared fresh daily.

2. ICB (initial calibration blank)

The ICB is 0.25 M NaOH solution and follows the ICV at the beginning of each Lachat run. If the absolute value of the ICB is not IRL or ± CRDL **or ½ the CRDL for Navy Projects**, the analyst's supervisor should be consulted before proceeding.

3. CCV (continuing calibration verification) **From primary std. that curve is made from.**

   The CCV will be analyzed after every 10 samples and at the end of the tray. The sampling of the CCV's will be done automatically by the Lachat if it is included in the tray definition. The CCV scheduling can be done under the Data Quality Management option in the Tray Definition screen. If the CCV is not within ±10 percent of its true value a CHK STD failure signal will be given by the Lachat and the analyst's supervisor should be consulted before proceeding.

4. CCB (continuing calibration blank)

   This sample verifies the instrumental baseline. If the absolute value of the CCB is not below the minimum detection limit the analyst's supervisor should be consulted before proceeding.

C. Calibration Approval:

For a cyanide calibration to be approved, segment (A-F) of the curve must have a correlation of at least 0.995 in chord 3.

D. Method Detection Limit (MDL), Empirical Laboratories Reporting Limit (ERL), Contract Required Quantitation Limit (CRQL) and Analyte Wavelength:
(MDLS are performed annually or whenever a change in the method is made.)

TABLE I

Aqueous and Soil Method Detection Limits(MDL), Empirical Laboratories Reporting Limits(ERL), CLP OLM04.1 & OLM05.2 Contract Required Quantitation Limits (CRQL)

Analytes by EPA 335.1, 335.3, 9012A , SOW 4.1 & 5.2	AQUEOUS MDL(ug/L)	AQUEOUS ERL(ug/L)	AQUEOUS CRQL ILMO 4.1 (ug/L)	AQUEOUS CRQL ILMO 5.2 (ug/L)	SOLID/SOIL MDL (mg/Kg)	SOLID/SOIL ERL (mg/Kg)	SOLID/SOIL CRQL ILMO 4.1 (mg/Kg)	SOLID/SOIL CRQL ILMO 5.2 (mg/Kg)
Cyanide	0.0050	0.005	10	10	0.007	0.13	1	1

TABLE II

ANALYTE WAVELENGTH	
Cyanide	**570.0**

XI. CORRECTIVE ACTIONS

A. INSTRUMENT RELATED

1. ICV not within ± 10%

   a. If the problem is with the solution.

      i. Reprepare, obtain new stock if necessary.

   b. If the problem is with the calibration.

      i. Recalibrate thru analysis of appropriate standards and recheck ICV.

2. CCV not within ± 10%

   a. If the problem is with the solution.

      i. Reprepare, obtain new stock if necessary.

   b. If the problem is with the calibration.

      i. Recalibrate thru analysis of appropriate standards and reprepare/reanalyze the previous ten sample according the following guidelines.

         a. If the CCV was biased high, any of the previous ten samples which were BMDL do not require reanalysis.

         b. If the CCV was biased low, the previous ten samples must be reanalysed.

3. Ending CCB not ± RL or CRDL **or ½ the CRDL for Navy Projects**

   a. If the CCB is biased high.

      i. Any samples BDL or greater than 5X the CCB bias need not be reanalyzed.
      ii. Any samples above the detection limit but less than 5X the CCB level must be reanalyzed after the problem is corrected.

   b. If the CCB is biased low.

      i. Any samples greater than 5X the absolute CCB bias need not be reanalyzed.
      ii. All other samples must be reanalyzed after the problem is corrected.

B. DIGESTION RELATED

1. The preparation blank is not less than the ± RL or CRDL **or ½ the CRDL for Navy Projects**.

   a. If the problem with the instrument.

      i. Analyze a CCB to determine this.
      ii. If the problem was with the instrument correct the situation and reanalyze the preparation blank.

   b. If the problem is with the distillation.

      i. All associated samples which are BMDL or have a level of cyanide greater than 5X the level found in the preparation blank can be reported. If the level of cyanide in an associated sample is not BMDL nor greater than 5X the level found in the preparation blank, the sample must be redistilled/reanalyzed or reported as qualified. The project manager or QA manager will make this determination.

2. LCS not within our in-house generated control limits (or ±20%).

   a. If the problem is with the instrument.

      i. Reanalyze when instrument is in control.

   b. If the problem is with the digestion.

      i. If biased low, associated samples must be redigested.
      ii. If biased high, the impact upon the data user must be evaluated. The samples will be redigested or the data will be qualified on the final report.

3. Distilled check standard not within control limits of ±15%.

   a. If the problem is with the instrument.

      i. Reanalyze when instrument is in control.

   b. If the problem is with the digestion.

      i. If biased low, associated samples must be redigested.
      ii. If biased high, the impact upon the data user must be evaluated. The samples will be redigested or the data will be qualified on the final report.

C. SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20%

i. The associated sample data must be qualified on the final report.

2. Spike analysis recovery not within ±25%

   i. If the analyte level in the sample is greater than 4X the spiking level, the %recovery can not be evaluated and no action is taken.

   ii. If the analyte level in the sample is not greater than 4X the spiking level, the associated sample data must be qualified on the final report.

XII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIII. SOURCES/REFERENCES:

1. Lachat manual; Quick Chem method 10-204-00-1-A.

2. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983, Method 335.4.

3. Standard Methods for the Examination of Water and Wastewater, 14th Edition, APHA-AWWA-WCPC, Park 413D, pp. 370-372.

4. SW-846, 9012A, Revision September 1986.

5. U.S. Environmental Protection Agency, C.L.P. S.O.W. ILMO 4.1.

6. QuickChem AE, Automated Ion Analyzer Training Manual, Lachat Instruments.

7. QuickChem AE, Automated Ion Analyzer Software Reference Manual, Lachat Instruments.

Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

The following is a list of changes for sample preparation when the 5.2 statement of work is required:

1. The ICV shall be distilled.

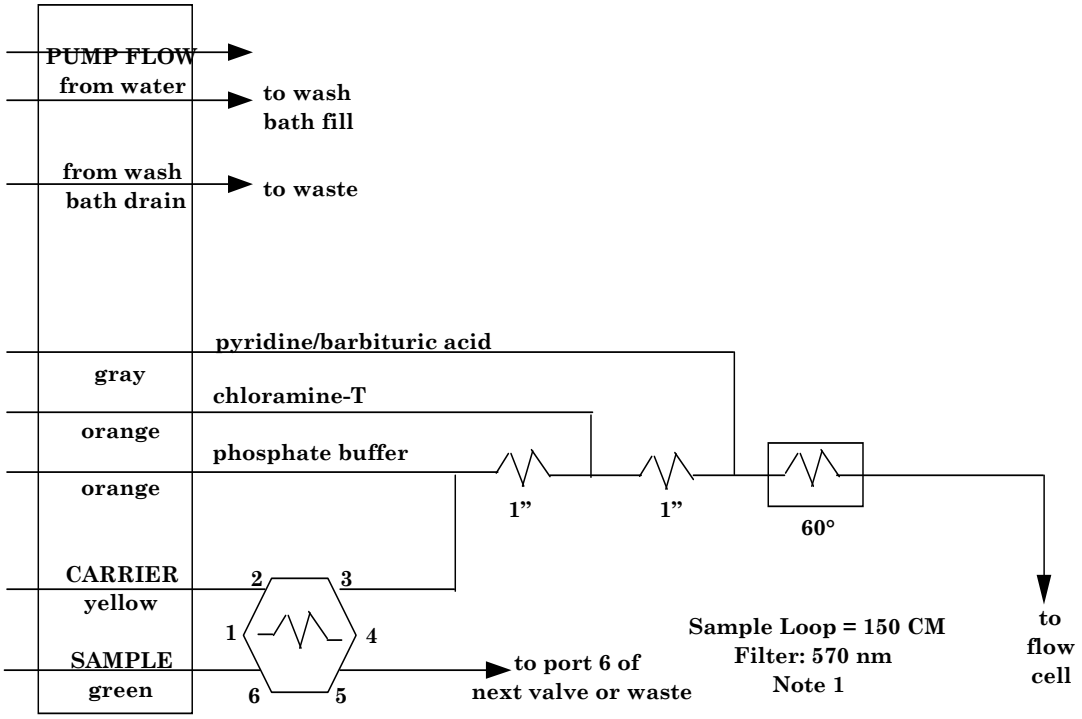
2. Boiling chips are to be added to each sample. Midi-Distillation is reflux 1.5 hours then the heat and vacuum is turned off and the samples cool an additional 15 minutes.

3. The QC criteria for both the Distillation Check QC and the distilled ICV is ±15%.

4. A CRI is required at the beginning and end of each run and for every 20 samples. The QC criteria for the CRI is ±30%.

5. Rounding rule for the appropriate level of precision is that the figure following those to be retained is $\geq$ 5, round up: otherwise round down. (examples: 1.5 and 2.5 would be 2 and 3 respectively rounded up; 1.4 and 2.4 would be 1 and 2 respectively rounded down) Please see Exhibit B, Section 3, (3.3.9.1) of SOW ILM0 5.2 for more guidance on rounding significant figures.

MANIFOLD DIAGRAM



CARRIER is 0.25 M Sodium Hydroxide

1" is 70.0 cm of tubing on a 1 in coil support

APPARATUS: Standard valve, flow cell, and detector head modules are used. The box shows 650 cm of heated tubing.

All manifold tubing is 0.8 mm (0.032 in) i.d., This is 5.2 µL/cm.

Note1: A 3.0 m x 0.022" id back pressure loop is placed at the exit of the flow cell.

Manifold Diagram Revision Date: 13 May

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):	
Batch Number(s):	
Method:	**9012A (Cyanide)**

QA/QC Item	Yes	No	NA	Second Level Review
1. Were samples analyzed within USACE holding times?				
2. Was initial calibration curve QC criteria met?				
3. Was all continuing calibration criteria in control?				
4. Did any sample exceed the highest calibration standard? (If yes, were appropriate dilutions made to generate samples concentration within calibration range?)				
5. Did LCS or blank spike meet control limits?				
6. Did MS/MSD meet control limits?				
7. Was the preparation (Method) Blank below the project required detection limits?				
8. Did you return samples back to cold storage immediately after use?				
9. Was distillation temperature monitored/documented and did you apply the thermometer correction factor?				
10. Sample preparation information is correct and complete.				
11. Analytical results are correct and complete.				
12. The appropriate SOP's have been used and followed.				
14. "Raw data" including all manual integration's have been correctly interpreted.				
15. "Special" sample preparation and analytical requirements have been met.				
16. Documentation complete (e.g., all anomalies in the analytical sequence have been documented, corrective action forms are complete.				

ANALYST DATA REVIEW CHECKLIST
9012A (Cyanide)

Comments on any "No" response:

_____
_____
_____
_____
_____
_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

Empirical Laboratories, LLC

ELECTROMETRIC DETERMINATION OF pH

METHODS
(USEPA) 150.1, Standard Methods 4500-H^+B AND 9040B FOR WATERS, LIQUIDS AND LIQUID WASTES, 9045C FOR SOILS AND SOIL WASTES

SOP NUMBER: **SOP-187**

REVISION NUMBER: **6**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: **09/05/06**

DATE OF LAST REVIEW: **02/08/08**

Empirical Laboratories, LLC

ELECTROMETRIC DETERMINATION OF pH

I. SCOPE AND APPLICATION:

A. This SOP is specifically for the Orion 420A pH meter with Orion Triode pH electrode.

B. USEPA Method 150.1/SM4500-H^+B is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain.

C. Method 9040B is applicable to aqueous wastes and those multiphase waste where the aqueous phase constitutes at lease 20% of the total volume of the waste. This method also fulfills the requirement for characterization of Corrosivity according to SW846.

D. Method 9045C is applicable to soils and waste samples. Wastes may be solids, sludges, or non-aqueous liquids. If water is present, it must constitute less than 20% of the total volume of the sample.

II. METHOD SUMMARY:

The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or combination electrode.

III. SAMPLE HANDLING AND PRESERVATION:

A. pH, when used for permit reporting on water samples, is intended to be a field test. It is often monitored on a continuous basis when 24 hour composites are collected. If the pH is to be analyzed on a discreet grab sample, most States require that analysis occur within 15 minutes of collection to be reported without qualification for regulatory purposes. Nevertheless, occasionally, samples will be transported to the laboratory for analysis. Frequently this is done for the information purposes only, to be used by the client or the laboratory for the purposes other than regulation. To avoid confusion or misuse of the data, these analyses will clearly be labeled as "laboratory pH" on the final report. They must be analyzed as soon as possible in the laboratory. Soil or solid samples are subject to the sample holding time restrictions, and should also be analyzed as soon as possible and qualified on the final report.

B. High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.

C. Samples must be unpreserved.

IV. INTERFERENCES:

A. The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or high salinity.

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

C. Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gently wiping the electrode or washing it with a detergent followed by rinsing with distilled water. An additional rinsing with dilute Hydrochloric Acid (1:10) may also be necessary to remove any remaining film.

D. Temperature fluctuations will cause measurement errors, however pH measurements made with the Orion 420A meter and the Orion Triode electrode have automatic temperature compensation features.

E. A dirty electrode may also cause problems. See the maintenance sections or the electrode manual.

V. EQUIPMENT/APPARATUS:

A. pH meter: This SOP is specifically for the Orion 420A. This meter has set-up features which have been pre-set. In order to change these, refer to the instruction manual, pages 8-9. This meter has an automatic temperature compensation feature.

B. Electrode: There are many different types of pH electrodes available. This SOP is for the Orion Triode pH electrode which has an epoxy outer body and contains an internal filling solution of Ag/AgCl.

NOTE: REFER TO THE INSTRUCTION MANUAL FOR ANY QUESTIONS OR PROBLEMS WITH EITHER THE METER OR THE ELECTRODE. ALSO REFER TO THE INSTRUCTION MANUAL FOR PROPER CARE AND MAINTENANCE OF THE pH METER AND PROBE.

C. Magnetic stirrer and Teflon-coated stirring bars. Put a piece of cardboard between the stirrer and the beaker containing the sample so that the heat from the stirrer will not affect the temperature of the sample.

D. Small beakers or cups.

Empirical Laboratories, LLC

VI. REAGENTS:

A. Standard buffers: 4, 7, and 10. The pH meter must be calibrated using standard buffers daily or, if not daily, with each use. Separate solutions of the three buffers should be kept in 120 ml. plastic bottles with the caps on when not in use. Pour up fresh buffers each use. (Record the date in the log book).
An additional pH 12 buffer is required for the Corrosivity test of alkaline wastes per Method 9040B.

B. Reference electrode filling solution.

1. Use Orion #900011 which contains AgCl. Make sure that the filling solution is the correct one for your electrode. If you use the wrong solution you may damage the electrode.

2. Never allow the electrode to dry out.

3. Change the filling solution at least once a month. (Record the date in the log book). When you change the filling solution you should soak the electrode in pH 7 buffer for at least one hour before analyzing samples.

C. Deionized water.

D. Hydrochloric acid (HCl): 1:3 mixture with reagent water.

VII. CALIBRATION:

A. Initial calibration (2 point)

This meter is capable of both autocalibration and manual calibration. We calibrate manually.

1. Turn the power on. It will display a quick check mode and then the reading will stabilize. The meter should be in the pH mode, if not, press the "mode" key until the pH mode indicator is displayed.

2. Uncover the hole on the upper part of the electrode. This allows a uniform flow of the filling solution. (It should be kept covered when not in use.)

3. Rinse the electrode with deionized water and blot dry with a kimwipe (do not wipe the electrode).

4. The meter must be calibrated prior to use with two pH buffer standards which bracket the expected value of the sample to be

measured (4 and 7, or 7 and 10). Place the electrode in pH 7 buffer first, with stirring bar turning. Make sure the electrode is not touching the bottom or sides of the beaker. Buffers must be at room temperature.

5. Press the "2nd" key, followed by the "cal" key. It will display the time and date of the last calibration and then "P1" will be displayed in the lower field -- this means it is ready to read the first calibration standard.

6. Wait for a stable pH display and the meter will say "ready". Press the "no" key. The first digit will start flashing. Scroll up or down using the arrow-head keys until the correct value appears in the first digit (it will be 7 for the 7.00 buffer) then press "yes". Continue in the same manner until all the digits have been correctly entered, then press "yes" to enter the new value. The display will remain frozen for a few seconds, then "P2" will be displayed which means that the meter is ready to read the second calibration standard.

NOTE: Due to the temperature compensation of the meter, at 20° C the 7 buffer should read 7.01.

7. Rinse the electrode and place in the pH 4 **or** 10 buffer (depending on the expected pH of the sample to be analyzed) with stirring bar turning. Wait for a stable pH reading and then enter the correct value as you did for the 7 buffer.

NOTE: As with the 7 buffer, due to the temperature compensation of the meter, at 20° C the 4 buffer should read 4.00 and the 10 buffer should read 10.05.

8. After both points have been calibrated, the electrode slope will be displayed in the main field. The slope should be between 92 and 102. (Record the slope on the data sheet.) If it is not within this boundary you should inspect the electrode and meter and recalibrate with fresh buffers. If the slope is still out of range, check the manual for troubleshooting.

9. The meter will automatically advance to the "measure" mode and you are now ready to check the calibration and read the samples.

B. Calibration for Corrosivity characterization by Method 9040B

1. For corrosivity characterization, the calibration of the pH meter should include a buffer of pH 2 for acidic wastes and a pH 12 buffer for caustic wastes; also, for corrosivity characterization, the sample must be measured at 25±1 °C if the pH of the waste is above 12.0. Repeat adjustments on successive portions of the two buffer solutions until

readings are within 0.05 pH units of the buffer solution value. The specific steps to follow match the explanations in Section A.

C. Calibration Check

1. Rinse the electrode and place it in the 7 buffer. Read this buffer as a sample and not as a calibration standard. Press "measure". The display will start to fluctuate as the pH is being measured. Once the reading stabilizes the meter will beep and the display will freeze.

2. Record the reading. (It should be 7.00± 0.09. If it is not within this range, inspect the electrode and meter and recalibrate with fresh buffers. If the reading is still out of range, check the manual for troubleshooting.)

3. If the 7 buffer reads correctly, read the 4 buffer and 10 buffer. Record these readings. (The reading should not deviate from the true values by more than 0.09 units. If they are not within this range, inspect the electrode and meter and recalibrate with fresh buffers. If the reading is still out of range, check the manual for troubleshooting.)

VIII. PROCEDURE:

A. Water and Liquid Waste Samples (Non Drinking Water) by Methods 150.1 or 9040B

1. Sample(s) should be at room temperature when analyzed. The Triode electrode is capable of adjusting for temperature inconsistencies, however, you should still adjust the samples to room temperature before analyzing. (Record the temperature of **each** sample on the data sheet.)

2. Rinse the electrode with deionized water and blot it dry with a kimwipe. Place it into the sample with the stirring bar turning. Make sure that the electrode does not touch the sides or the bottom of the beaker.

3. The display will start to change. Once the reading stabilizes the meter will beep and the number will freeze. Record this number on the data sheet.

4. If you calibrated with 7 and 4 buffers, the sample pH must fall between 7 and 4. If the pH falls out of this range, you must go back and recalibrate using the 7 and 10 buffers and rerun the sample.

5. If you are determining Corrosivity by 9040B, use a pH 12 buffer to bracket the alkaline upper range.

6. Be sure you rinse off the electrode with deionized water in between samples.

B. Drinking Water and Acid-rain Samples by Method 150.1

Treat these samples exactly as you would other water samples except for the stirring. It is imperative that the stir plate is set on its' lowest setting and that the sample is not stirred vigorously. You should use the smallest stir bar possible. Make sure that you do not aerate the sample.

C. Soil Samples by Method 9045C

1. To 20 g of soil in a 50-mL beaker, add 20 mL of reagent water, cover, and continuously stir the suspension for 5 minutes. Additional dilutions are allowed if working with hygroscopic soils and salts of other problematic matrices.

2. Let the soil suspension stand for about 1 hour to allow most of the suspended clay to settle out from the suspension or, if necessary, filter or centrifuge off the aqueous phase for pH measurement.

3. Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint.

4. Solutions should be a room temperature when analyzed. The Triode electrode is capable of adjusting for temperature inconsistencies however, you should still adjust the samples to room temperature before analyzing. (Record the temperature of **each** solution on the data sheet.)

5. Rinse the electrode with deionized water and blot it dry with a kimwipe. Place it into the solution as described in step 3.

6. The display will start to change. Once the reading stabilizes the meter will beep and the number will freeze. Record this number on the data sheet.

7. If you calibrated with 7 and 4 buffers, the sample pH must fall between 7 and 4. If the pH falls out of this range, you must go back and recalibrate using the 7 and 10 buffers and rerun the sample.

8. Be sure you rinse off the electrode with deionized water in between samples.

B. Solid Waste Samples by Method 9045C

1. To 20 g of waste sample in a 50-mL beaker, add 20 mL of reagent water, cover and continuously stir the suspension for 5 minutes. Additional dilutions are allowed if working with hydroscopic wastes and salts or other problematic matrices.

2. Let the waste suspension stand for about 15 minutes to allow most of the suspended waste to settle out from the suspension or, if necessary, filter or centrifuge off aqueous phase for pH measurement.

NOTE: If the waste is hygroscopic and absorbs all the reagent water, begin the experiment again using 20 g of waste and 40 mL of reagent water.

NOTE: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned (Step IV.C) if it becomes coated with an oily material.

3. Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint.

4. Solutions should be a room temperature when analyzed. The Triode electrode is capable of adjusting for temperature inconsistencies, however, you should still adjust the samples to room temperature before analyzing. (Record the temperature of **each** solution on the data sheet.)

5. Rinse the electrode with deionized water and blot it dry with a kimwipe. Place it into the solution as described in step 3.

6. The display will start to change. Once the reading stabilizes the meter will beep and the number will freeze. Record this number on the data sheet.

7. If you calibrated with 7 and 4 buffers, the sample pH must fall between 7 and 4. If the pH falls out of this range, you must go back and recalibrate using the 7 and 10 buffers and rerun the sample.

8. Be sure you rinse off the electrode with deionized water in between samples.

IX. ELECTRODE STORAGE AND MAINTENANCE:

A. Storage

1. Store the electrode in a solution made up of 1 gram KCl or NaCl in 200 mL of pH 7 buffer. This solution may be purchased from Fisher.

2. The reference chamber hole should be covered overnight and the power to the pH meter should be turned off.

3. White crystals will probably form on the electrode. These are from the potassium chloride and will not damage the electrode, however, the electrode should be rinsed with distilled water to get rid of this build-up.

4. If storing the electrode for more than one week, the reference chamber should be filled and the fill hole should be securely covered. Cover the sensing element with its protective cap containing a few drops of storage solution. Before reusing it, prepare it as a new electrode. (See manual).

B. Maintenance

1. Drain the reference chamber, flush it with fresh filling solution and refill the chamber. Allow the electrode to set overnight before using it. This should be done on a monthly basis. Record the date in the log book.

2. Inspect the electrode for scratches, cracks, salt crystal build-up, and general physical integrity.

3. If there is build-up of salt or any grease or dirt on the electrode it may be necessary to soak it in dilute HCl (1:10) for half an hour. Then drain and refill the reference chamber and soak the electrode in storage solution for at least half an hour before using. Also record this in the log book.

For more information on storage and maintenance of the electrode, see the instruction manual.

X. QUALITY CONTROL:

A. Analyze a laboratory control sample (LCS) or second-source standard once a month or every 300 measurements, whichever is more frequent. The tolerance range is ± 0.25 units.

B. Run a duplicate every 10 samples (count frequence per method and matrix). The specification limit is ± 0.09 units. If exceeded, repeat the measurement once or twice more. If the specification is still not met, you must recalibrate and reanalyze the sample in question.

C. Read one of the buffers every 20 samples (all methods and matrices included to count frequency), or at the beginning and end of the

measurement session; whichever is more frequent. If it does not read its true value ± 0.09 units, then you must recalibrate.

D. Record the QC data (LCSs and duplicates) on the QC sheet. Make sure that this information is written legibly and is complete, including specification of the method number.

E. Electrodes must be rinsed thoroughly between samples.

F. Document any problem experience during the measurements. Complete a corrective action where necessary. This must be done within 24 hours of occurrence of the incident.

G. Refer to SOP-431 for common environmental laboratory definitions.

XI. REFERENCES

A. USEPA Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983, Method 150.1.
B. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Methods 9040B and 9045C.
C. Standard Methods 18th Edition 1992 p. 4-65.

XII. WASTE MANAGEMENT AND POLLUTION PREVENTION

A. Please see Waste Disposal SOP-405 for instruction of proper disposal of waste generated from this area.

B. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

Empirical Laboratories, LLC

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

METHOD 1311

SOP NUMBER: **SOP-198**

REVISION NUMBER: **5**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: **02/09/06**

DATE OF LAST REVIEW: **02/08/08**

Empirical Laboratories, LLC

METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

2.0 SUMMARY OF METHOD

2.1 For a highly liquid waste, determine if the percent dry solids is less than 0.5%. If so, the sample is filtered and the filtrate is treated as the extraction fluid. If not, the sample is reduced in size to pass through a 9.5 mm sieve. The percent wet solids are then determined. A 5 g and 100 g aliquot of wet solids are generated. The liquid phase for the 100 g aliquot is stored at 4 degrees Celsius. The 5 g aliquot is used to determine the appropriate extraction fluid. The 100 g aliquot is added to the extraction fluid and tumbled for about 18 hr's. The sample is filtered and the pH of the fluid is determined. An appropriate amount of the liquid phase is added to the extraction fluid and the sample is preserved according to the test, which will be performed.

2.2 The TCLP extract for volatiles is analyzed by method 8260B according to SOP ATSD-202. The TCLP extract for semivolatiles is subject to separatory funnel extraction by method 3510 according to SOP ATSD-300. The TCLP extract for metals is divided for two separate digestions and analyses: (a) mercury digestion and analysis by 7470A (ATSD-103), and (b) ICP-metals digestion by 3010A (ATSD-100) and analysis by 6010B (ATSD-116).

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods and related SOPs. (See section 2.2)

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion at 30 $\pm$ 2 rpm. This rate is measured and recorded with each extraction to ensure accuracy of the equipment.

4.2 Extraction Vessels

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4.2.1 Zero-Headspace Extraction Vessel (ZHE). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel. The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 30 to 40 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 10 minutes, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure. Whereas the volatiles procedure refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds.

4.2.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste. It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood or well ventilated area.

4.3.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

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[1] VITON® is a trademark of Du Pont.

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 µm (Whatman GF/F), or equivalent. **Pre-filters must not be used. When evaluating the mobility of metals**, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.20.

4.6 ZHE Extract Collection Devices: TEDLAR®[2] bags are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device, only when both liquid and solid phases exist. Collect final extract in a 40 mL vial when only a solid phase exist.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see Section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, various sizes.

4.10 Watchglass

[2] TEDLAR® is a registered trademark of Du Pont.

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4.11 Magnetic stirrer.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods.

5.2.1 A water purification system may also be used to generate reagent water for volatile extractions.

5.2.2 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 $\pm$ 5 degrees C, bubble a contaminant-free inert gas (e.g. nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.3 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.4 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.5 Sodium hydroxide (15N), NaOH, made from ACS reagent grade.

5.6 Glacial acetic acid, CH_3CH_2COOH, ACS reagent grade.

5.7 Extraction fluid.

5.7.1 Extraction fluid #1: Add 11.4 mL glacial acetic acid to approximately 1800 mL DI water. Add 8.6 mL 15N sodium hydroxide and dilute to 2 L. Seal and invert four times. Determine the pH which should be 4.93 +/- 0.05. Record in appropriate reagent log (RL) notebook.

5.7.2 Extraction fluid #2: Add 11.4 mL glacial acetic acid to approximately 1800 mL DI water and dilute to 2 L. Seal and invert four times. Determine the pH which should be 2.88 +/- 0.05. Record in appropriate reagent log (RL) notebook.

NOTE: All extraction fluids are purchased “certified” or prepared fresh and in volume quantity that matches the number of TCLP extractions to be performed on a given day. The TCLP/SPLP log-book is used to record the fluid type of choice with indication of its traceability to the lot numbers of acetic acid and sodium hydroxide used.

5.8 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Extreme care must be taken when taking samples. Samples should be collected using an appropriate sampling plan.

6.2 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction. If volatile organics are of concern, another aliquot may be needed.

6.3 Preservatives will not be added to samples before TCLP extraction.

6.4 For volatiles, the samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4°C. Samples should be opened only immediately prior to TCLP extraction).

6.5 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. **Extracts must be spiked according to their prospective analytes before preservation. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Section 7.2.14 if precipitation occurs).** Extracts or portions of extracts for volatile analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. Preserve according to the analytical methods as referenced in 2.2.

7.0 PROCEDURE

7.1 Preliminary Evaluations

Perform preliminary evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids; (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration; (3) determination of whether the solid portion of the waste requires particle size reduction; and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste.

7.1.1 Percent wet solids: Percent wet solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure.

7.1.1.1 If the sample will obviously yield no liquid when subjected to pressure filtration proceed to Section 7.1.3.

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7.1.1.2 If the sample is liquid or has more than one phase, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the weighed filter in the buchner funnel.

7.1.1.5 Mix the sample and weigh out a representative subsample of (100 gram minimum) and record exact weight.

7.1.1.6 Allow sludges to stand to permit the solid phase to settle.

7.1.1.7 Quantitatively transfer the sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, this material may not filter. If this is the case, the material

within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances.

7.1.1.9 Remove filter carefully from the buchner funnel so as to get as much of the solid as possible.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent wet solids} = \frac{(\text{Filter wt.} + \text{sample wt.}) - \text{filter wt.}}{\text{Total weight of waste}} \times 100$$

7.1.2 If the percent solids is equal to or greater than 0.5%, then proceed either to Section 7.1.3 to determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid material and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid material at 100 $\pm$ 20°C. Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{(\text{Wt. of dry waste} + \text{filter}) - \text{tared wt. of filter}}{\text{Initial wt. of waste}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction: Using the solid portion of the sample, evaluate the solid for particle size. Particle size reduction is required, unless the solid passes through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the

waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken.

NOTE: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents, determine the appropriate fluid for the nonvolatiles extraction as follows:

NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1. Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 250 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH is >5.0, add 3.5 mL 1N HCl, **slurry briefly**, cover with a watchglass, heat to 50°C, and hold at 50°C for 10 minutes. (Note: Do not mix the sample during heating). The hot block may be used for the purpose of heating and holding at 50°C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature (use Hobart to aid in cooling, 30 to 60 minutes) and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Note: The pH must be measured as quickly as possible in the phase of the procedure. It is critical to measure the pH as soon as the sample has reached room temperature. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation was determined to be 100% solid, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain).

7.2 Procedure for Metals and Semi-Volatiles

A minimum sample size of 100 grams (solid and liquid phases) is recommended. If less than the specified amount is used, proportion extraction fluid accordingly and notify manager. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes

of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required.

All glassware and equipment must be thoroughly cleaned before use. A hot soapy water wash, rinse with tap water, then repeat following with a DI water rinse. Rinse with 1:1 HNO_3 , acetone, and a final rinse with DI water.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.2.4 to 7.2.8.

7.2.3 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 4.4).

7.2.4 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids, the liquid portion, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required. For wastes containing >0.5% dry solids use the percent solids information to determine the optimum sample size (100 gram minimum) for filtration.

7.2.5 Allow sludges to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered, followed by filtration of the solid portion of the waste through the same filtration system.

7.2.6 Refer to Section 7.1.1.7.

7.2.7 Refer to Section 7.1.1.8.

7.2.8 If the waste contains <0.5% dry solids, proceed to Section 7.2.13. If the waste contains >0.5% dry solids, and if particle size reduction of the solid was needed in Section 7.1.3, proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.9 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.

7.2.10 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \text{ x percent wet solids x weight of waste fltered}}{100}$$

Slowly add this amount of appropriate extraction fluid to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature shall be maintained at 23 $\pm$ 2 □C during the extraction period. Record both tumble rate and room temperature.

NOTE: As rotation continues, pressure may build up within the extractor bottle for some types of wastes. To relieve excess pressure, the extractor bottle should be periodically opened (e.g., after 15 minutes, and 30 minutes) and vented into a hood.

7.2.11 Following the 18 $\pm$ 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed.

7.2.12 Prepare the TCLP extract as follows:

7.2.12.1 If the sample contained no initial liquid phase, the filtered liquid material obtained is defined as the TCLP extract. Proceed to Section 7.2.13.

7.2.12.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.13.

7.2.12.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.11, do not combine these liquids. Analyze these liquids, collectively defined as the

TCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.1.3 Following collection of the TCLP extract, the pH of the extract must be recorded. Immediately split aliquots, give to appropriate analyst for spiking and preservation of the extract for analysis. Metal aliquots must be acidified with nitric acid to pH <2. (If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible.) All other aliquots must be stored under refrigeration (4°C) until analyzed. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. Refer also to sections 2.2 and 6.5.

If the individual phases are to be analyzed separately, determine the volume of the individual phases (to $\pm$ 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = On next page
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3 Volatiles Extraction Procedure

Use ZHE device to obtain TCLP extract for analysis of volatile compounds only.

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

All glassware and equipment must be thoroughly cleaned before use. A hot soapy water wash, rinse with tap water, then repeat following with a DI water rinse. Rinse with methanol and a final rinse with DI water.

7.3.1 Pre-weigh the filtrate collection container and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 7.3, Section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100% solid, weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Section 7.3.5.

7.3.4 If the waste contains < 0.5% dry solids, the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing $\geq$ 0.5% dry solids, use the percent solids information determine the optimum sample size to charge into the ZHE.

The recommended sample size is as follows:

7.3.4.1 For wastes containing < 5% solids, weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing $\geq$ 5% solids, determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent wet solids}} \times 100$$

7.3.5 If particle size reduction of the solid portion of the waste was required in Section 7.1.3, proceed to Section 7.3.6. If particle size reduction was not required in Section 7.1.3, proceed to Section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in Section 7.1.3. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

NOTE: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to Section 7.3.7.

7.3.7 Waste sludges need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

NOTE: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see Section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Section 7.3.12.

7.3.9 Attach the pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

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7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

(Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.)

If the original waste contained <0.5% dry solids, this filtrate is defined as the TCLP extract. Proceed to Section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately or preserved and stored at 4°C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \text{ x percent wet solids x weight of waste filtered}}{100}$$

7.3.12 The following details how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases.

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation apparatus and rotate at 30 $\pm$ 2 rpm for 18 $\pm$ 2 hours. Ambient temperature (i.e., temperature of room in which extraction

occurs) shall be maintained at 23 ± 2°C during agitation. Record both tumble rate and temperature.

7.3.13 Following the 18 ± 2 hour period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Section 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag or VOC vials) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Section 7.3.9. All extract shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase.

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from above is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from above and the initial liquid phase (Section 7.3.9) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis (one of the vials will be spiked at this point) and store with minimal headspace at 4°C and preserve with HCI until analyzed. Analyze the TCLP extract according to the appropriate analytical methods (refer to section 2.2). If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

8.0 QUALITY ASSURANCE

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8.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel. No bias correction is to be taken into consideration (Fr 57, 227).

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.). One matrix spike must be analyzed for each analytical batch. Follow the matrix spike addition guidance provided in each analytical method. (The method and SOPs are referenced in section 2.2.)

8.2.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation.

8.2.2 The matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than ten times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same volume of TCLP extract as that which was analyzed for the unspiked sample.

8.2.3 The matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. If interferences exist, an alternate approach may be required.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%Recovery) = 100\ (X_s - X_u)/K$$

where:

X_s = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.3 All quality control measures described in each analytical methods must be followed.

8.4 The use of method of standard addition (MSA) shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

8.4.1 The MSA requires preparing calibration standards in the sample matrix rather than reagent water. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The forth aliquot is the unknown. The first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the

sample. All four aliquots are maintained at the same final volume by adding reagent water. Analyze all four aliquots.

8.4.3 Prepare a plot, or subject data to linear regression, of instrument signals or external-calibration-derived concentrations as the dependant variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

8.5 TCLP extraction holding times.

SAMPLE MAXIMUM HOLDING TIMES [DAYS]				
	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semi-volatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable

If holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Of course, exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

GC/MS VOLATILES
BY EPA METHOD 624 AND
SW-846 METHOD 8260B
INCLUDING APPENDIX IX COMPOUNDS

SOP NUMBER: **SOP-202**

REVISION NUMBER: **20**

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: **01/11/08**

DATE OF LAST REVIEW **01/11/08**

GC/MS VOLATILES
BY EPA METHOD 624 AND SW-846 METHOD 8260B

1.0 SCOPE AND APPLICATION

Please see Appendix for definitions.
This SOP (based primarily on SW-846 Method 8260B) is used for the analysis of volatile organic compounds in a variety of matrices (soils, sediments, waters, etc.). Methods SW-846 Method 8000B; *Federal Register* Method 624; and CLP Method for Volatiles have also been used in the development of this SOP. The analyses by these various methods are clearly defined in the respective regulatory manuals. A good understanding of these different methods is essential to the performance of each method. The normal laboratory list of analytes with their typical LCS limits is found attached in the appendix. Other compounds may be analyzed by this SOP as detailed in section 1.0 of SW-846 Method 8260B. Any questions left by this SOP should be answered by reading the methods, paying close attention to SW-846 8000B/8260B, EPA 624 and CLP. If questions still remain unanswered, check with the Organic Lab Manager, QA/QC Officer and/or the Technical Director.

2.0 METHOD SUMMARY

After sample preparation, the sample is introduced into the GC/MS generally using purge and trap but sometimes using direct injection (see SW-846 Methods 5030B, 5035 and 3585 for preparation). In purge and trap, the analytes are stripped from the sample using helium and trapped on an adsorbent tube. The tube is heated while being backflushed with helium to carry the analytes to the GC/MS system. The analytes are separated in the gas chromatograph by a combination of the temperature program and the capillary column. The analytes are then detected by the mass spectrometer. Analytes are identified by comparing the mass spectra of known standards with the mass spectra of the sample. Analytes are quantitated relative to known standards using the internal standard method.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Section 3.0 and tables 3-1 and 3-2 of the Empirical Laboratories, LLC Quality Assurance Manual include details concerning sample preservation, containers and handling of volatile samples. All water and non-quarantined soil volatile samples are stored in the Hobart in the sample storage room at a temperature of 4°C. Quarantined soil volatile samples are stored in the dorm-size refrigerator in the sample receiving/log-in room at a temperature of 4°C. Non-preserved water volatile samples have a holding time of 7 days from date of sampling. Preserved water samples and soil volatile samples have a holding time of 14 days from date of sampling (unless otherwise specified for the project).

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Section 3.0 of SW-846 Method 8260B details interferences and potential problems which may be encountered when dealing with volatile analyses.

5.0. EQUIPMENT AND APPARATUS

5.1 GC : HP 5890 or 6890, temperature programmable, suitable for split or splitless injection.

5.2 Column: DB-VRX 60 meter x 0.25 mm I.D. 1.4 µm film thickness or 20 meter x 0.18 mm ID 1.0 µm film thickness silicon coated fused silica capillary column or equivalent.

5.3 M.S. : HP 5971, 5972 or 5973 capable of scanning 35 to 500 amu every one second or less, using 70 volts electron energy in electron impact ionization mode. The MS is capable of producing a mass spectrum for p-Bromofluorobenzene, BFB, which meets all tuning criteria for EPA methods [when 1 µL (50 ng) of the GC/MS tuning standard are injected through the GC.]

5.4 Purge and Trap Unit

5.4.1 Concentrators: Tekmar LSC 2000 or Tekmar/Dohrmann 3000/3100 Sample Concentrator equipped with Supelco trap number 2-1066-U or 2-4920-U VOCARB 3000 providing good delivery for all target compounds.

5.4.2 Autosamplers: Varian Archon 51 position programmable autosampler with 5ml to 25ml water and heated soil capability.

5.5 Acquisition Software: HP chemstation system interfaced to the GC/MS. The system acquires and stores data throughout the chromatographic programs.

5.6 Data Processing Software: TargetDB on Windows NT data system interfaced to the HP Chemstation. The system accepts and stores acquired data. It plots by extracted ion current profile (EICP). The system is also capable of integrating the abundances of any EICP between specified time or scan-number limits. The most recent NBS mass spectral library is installed.

5.7 Microsyringes – 1.0, 5.0,10, 25, 100, 250, 500 and 1000 µL.

5.8 Syringes – 5, 25 and 50 mL, gas-tight with Luer end.

5.9 Balance - analytical, 0.0001 g; top-loading, 0.1 g.

5.10 Disposable pasteur pipets.

5.11 Volumetric flasks, Class A - 2 mL, 5 mL, 10 mL, 50 mL, 100 mL and 250 mL with ground-glass stoppers.

5.12 Spatula - stainless steel.

5.13 Glass scintillation vials - 20mL with screw caps.

5.14 Nitrile Gloves

5.15 pH paper (measures pH from 0-14).

6.0 REAGENTS AND SOLUTIONS

6.1 Organic-free reagent water - obtained from a modulab system.

6.2 Methanol - Purge and trap grade (EM-Omnisolv EM-0482-6 or equivalent)

6.3 Methanol - suitable for use in gas chromatography (B&J Omnisolv MX0484-1, or equivalent)

6.4 Sodium bisulfate, $NaHSO_4$ – ACS reagent grade, or equivalent. Available from Aldrich (Part No. 30,782-3).

6.5 Stock standards are purchased in mixtures from reputable vendors. The date they are received is noted on the label. The date they are opened is noted on the label and recorded in the VOA standards and reagents logbook along with their lot number and vendor. Each standard that is prepared is recorded in the VOA standards and reagents logbook and given a sequential number. Each standard label is completed with the standard number, name, preparation date, expiration date, solvent and analyst initials. Stock standards, when opened, have an expiration date of 6 months except for gas standards for South Carolina samples which have a one week expiration date. All stocks and standards are stored in the freezer at a temperature of -15°C ± 5°C or less from the date they are received/prepared. The freezer temperature is monitored daily with an annually calibrated thermometer and recorded with calibration correction in the VOA refrigerator/freezer logbook. Makeup of common standards is detailed below. See the VOA standards log book for makeup of other standards.

6.5.1 The Bromofluorobenzene (BFB) tuning standard is prepared as follows: Using a 50µL syringe, 40µL of standard (BFB @ 2500ng/µL) is injected into a 2mL volumetric flask containing approximately 1.0mL P&T methanol (Vendor,Lot) and diluted to volume with same making a 50ng/µL standard. After capping and inverting 3 times, the solution is transferred to a labeled 2ml, teflon-lined, screw-capped vial and stored in the freezer at -15°C ± 5°C or less for up to 6 months(1 week for South Carolina samples). A direct injection of 1µL is used to tune the instrument.

6.5.2 The internal and surrogate standard is prepared as follows: Using the indicated syringe, the indicated amount of standard is injected into a 50 mL volumetric flask containing P&T methanol (Vendor,Lot) and diluted to volume with same making a 150ng/µL standard. After capping and inverting 3 times, the solution is transferred to the Archon standard vial and stored under helium for 1 month or less. Each 8260/624 sample is automatically injected with 1µL of this standard. The internal standard/surrogate solution will be replaced if the –50%-200% criteria fails in the CCV.

Standard	Conc. (ng/µL)	Syringe (µL)	Amount (µL)
8260 ISTD/Surr. Mix (Vendor,Lot)	2500	1000	3000

6.5.3 Calibration standards are prepared from the vendor stock standards at appropriate concentrations as follows. Occasionally unusual compounds are added to the mix so it is best to check the VOA standards log book for exact standard makeup. Note: for laboratory control spikes (LCS), alternate sources or lot numbers from the main calibration standard are used to make the LCS standard. See the appendix for analytes in the main mixes.

6.5.3.1 Primary Standard: Using the indicated syringe, the indicated amount of standard is injected into a 2mL volumetric flask containing approximately 1.0mL P&T methanol (Vendor,Lot) and diluted to volume with same to make a 100-500ng/µL standard. After capping and inverting 3 times, the solution is transferred into 2ml amber vial w/mini-inert valve and stored in the freezer at -15°C ± 5°C for 1 week. A 50µg/L (5mL purge) standard is made using 25µL of this standard to 50mLof reagent water.

Stock Standard(CCV)	Conc (ng/µL)	Syringe(µL)	Amount(µL)	Final Conc (ng/µL)
2-CEVE **(Cat#30265)** (Vendor, Lot)	20000	25	20	200
Vinyl Acetate **(#3766)** (Vendor, Lot)	5000	100	80	200
Ketones **(cat#30006)** (Vendor, Lot)	5000	100	80	200
Liquid mix **(C-349H-07)** (Vendor, Lot)	2000	100	100	100
Custom mix **(CCS-1037)** (Vendor, Lot)	5000	50	40	100
Gases **(cat#30042)** (Vendor, Lot)	2000	100	100	100
Acrolein/Acrylonitrile **(CC2098.10)** (Vendor, Lot)	20,000	50	50	500

Additional compounds may be added such as Appendix IX. Refer to standards log.

6.5.4 ICV/LCS/MATRIX SPIKE MIX: A second source standard is to check the validity of the gas and primary calibration standards used in analyzing the calibration curve. Using the indicated syringe, the indicated amount of standard is injected into a 2mL volumetric flask containing approximately 1.0mL P&T methanol (Vendor,Lot) and diluted to volume with same to make a 100-500ng/µL standard. After capping and inverting 3 times, the solution is transferred into 2ml amber vial w/mini-inert valve and stored in the freezer at -15°C ± 5°C for 1 week. A 50µg/L (5mL purge) ICV/LCS/Matrix Spike is made using 25µL of this standard to 50mLof reagent water/Sample Matrix.

Stock Standard(ICV/LCS)	Conc (ng/µL)	Syringe(µL)	Amount(µL)	Final Conc (ng/µL)
2-CEVE(Vendor,Lot#)	20,000	25	20	200
Vinyl Acetate(Vendor,Lot#)	5000	100	80	200
Ketones(Vendor,Lot#)	5000	100	80	200
Liquid mix (Vendor,Lot#)	2000	100	100	100
Custom Mix(Vendor,Lot#)	5000	50	40	100
Gases (Vendor,Lot#)	2000	100	100	100
Acrolein/Acrylonitrile (Vendor,Lot#)	50,000	50	50	500

7.0 PROCEDURE

7.1 Chromatographic conditions – Refer to corresponding instrument maintenance log for current gas chromatograph, mass spectrometer, and concentrator conditions.

7.2 System Bakeout - Prior to analysis, the autosampler purge and trap unit is stepped to bake and an instrument blank is analyzed.

NOTE: Further cleaning may be accomplished by backflushing the lines with methanol and then analyzing blanks overnight.

7.3 Tuning - Prior to any calibration or analysis, BFB tuning criteria must be met for a 1.0µL injection of the tuning standard [see below]. Tune must be met every 12 hours sample analysis is to be performed (every 24 hours for *Federal Register* Method 624 except for South Carolina which only allows 12 hours). The mass spectrum of BFB is acquired as follows: by using one scan at the apex peak, or by using the mean of the apex and the preceding and following scans or mean of a symmetric pattern of scans about the apex, or using the average across the entire peak. Background subtraction is accomplished using a single scan no more than 20 scans prior to the elution of BFB.

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

7.4 Calibration: Calibration standards are made up in water using the appropriate amount of the methanol standard. Calibration for soils for South Carolina requires that 5mL of sodium bisulfate solution is added to each calibration standard made if the samples will be preserved with sodium bisulfate. All calibration standard integrations must be checked for acceptability.

7.4.1 Initial Calibration - An initial calibration curve at no less than five concentration levels must be analyzed and shown to meet the initial calibration criteria before any sample analysis may be performed. For Arizona samples the surrogates must also be calibrated at a minimum of five concentrations. Method 624 requires that the %RSD be less than 35% to use the average response factor for quantitation, the curve is to be used otherwise and should have a correlation coefficient (***r***) of $\geq$0.995. Method 8260B requires that the %RSD be less than 15% to use the average response factor for quantitation, the curve is to be used otherwise as long as ***r*** is $\geq$0.995. In addition, there are calibration check compounds (CCCs) listed below which must have a %RSD less than 30% and five system performance check compounds (SPCCs) which must meet the average response factor criteria listed below. The lowest standard must be less than or equal to the reported quantitation limit and the highest standard must not exceed the linear range of the detector. Any manual integrations are documented by inclusion of the integrated signals initialed, dated, and reason with the quantitation report and chromatogram. Any response factors less than 0.050 must be supported by the mass spectrum of the lowest standard.

CCCs:	1,1-Dichloroethene	Toluene
	Chloroform	Ethylbenzene
	1,2-Dichloropropane	Vinyl chloride

SPCCs:	Chloromethane	0.10
	1,1-Dichloroethane	0.10
	Bromoform	0.10
	Chlorobenzene	0.30
	1,1,2,2-Tetrachloroethane	0.30

7.4.2 Initial Calibration Verification - A second source standard at the 50 µg/L (5mL purge) level is used to check the validity of the curve. The standard recovery for all analytes must be between 75 and 125%. If the second source recovery is above 125%, the main standard has probably deteriorated for that compound. That standard must be replaced and a new curve generated. If the second source recovery is below 75%, the second source standard has probably deteriorated for that compound and must be replaced. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram.

7.4.3 Continuing Calibration Verification (every 12 hours) - A midpoint calibration standard (generally 50 µg/L - 5mL purge) must be analyzed and calculated against the initial calibration curve, then shown to meet the calibration check criteria before any sample analysis may be performed. Acceptance criteria for method 8260B consists of the same SPCC criteria as

above and ≤20% drift or difference (calculations given in section 7.10) for the CCCs as listed above. The internal standards must also be evaluated as listed below. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram. Samples are then quantitated against the initial calibration curve. Note: If any compound in the continuing calibration not subject to the criteria above exceeds 30% D, it must be evaluated and initialed by the organic section manager. If deemed acceptable, the analyst may continue analysis.
NOTE: Acceptance criteria for method 624 consists of meeting recovery limits found in table 5 of the method for a QC check sample. This QC check sample is made from a separate source or lot number than the calibration standard at a concentration of 20 µg/L.

Internal standard checks

7.4.3.1.1 Retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.3.1.2 Response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 LCS - An LCS is analyzed every 12 hour tune.Using standards prepared from an alternate vendor or lot number, blank water is spiked at the 50 µg/L (5mL/soil) or 10 µg/L (25mL) level. See section 8.3 below for criteria and corrective action. Note: the concentration of the LCS will be 20 µg/L when analyzing 624 samples (QC Check Sample).

7.6 Method Blank - Prior to sample analysis, the system must be shown to be free of contamination through analysis of a method blank. See section 8.4 below for criteria and corrective action.

7.7 Sample Analysis - Prior to analysis, the samples are prepared for chromatography using the appropriate sample preparation method (5mL water, 25mL water, low soil, high soil, etc.) See SOP-225 for preparation of a 5035 soil sample. For a 5mL/25mL water sample, use the following procedure:

7.7.1. Load the vial into the Archon autosampler in the expected position.

7.7.2. Program the Archon for the loaded vial range and necessary dilutions, making sure the programmed method is set for the same volume as the purge vessel on the front of the LSC 2000 or 3000/3100 and that the Chemstation sequence matches the Archon sequence. Note: TCLP samples are analyzed at a 10x dilution. One TCLP sample is spiked per matrix.

7.7.3. After analysis of the sample has been completed, check the pH of the sample using pH paper and verify it to be less than a pH of 2. If it is not, record the pH and generate a corrective action report. The sample report will have to be flagged for preservation if the analysis is being performed more than 7 days after sampling. [Note: TCLP samples do not require a pH check.]

7.8 Instrument sequence

An example of a typical instrument sequence log follows:

1-BFB Tune (12:00 am)
2-CCV
3-LCS
4-Method Blank
5-Sample
6-Sample
7-Sample
8-Sample
9-Sample
10-Sample
11-Sample
12-Sample
13-Sample
14-Sample
15-Sample
16-Sample
17-Sample MS
18-Sample MSD
19-BFB (12:00pm - 12 hours since last BFB/CCV)
20-CCV
21-LCS
22-Method Blank
23-Sample
24-Sample

7.9 Data Reduction/Evaluation - Each sample analysis sequence is documented using the computer run log generated on the chemstation. This run log is signed, dated and paginated then placed in a 3 ring binder for that instrument. After the sample has been analyzed, the data is processed through the TargetDB on Windows NT data system. Quantitative measurements are performed using the calculations found in section 7.10 below. The following must be checked to determine if the sample will need any reanalysis or dilution. Formal data evaluation is detailed in SOP-200 (documented using the USACE Analyst Data Review Checklist for USACE projects).

7.9.1 Internal Standards - Areas should be within 50 to 200 percent of the area of the continuing calibration. Retention time should be within 30 seconds of the retention time of the continuing calibration. Note: criteria applies to the continuing calibration, not samples, but is used as an indication of the sample analysis validity. If not, the sample and historical data should be evaluated to determine the cause of the problem. Reanalysis is expected if it appears to be from a leak. If matrix effect is confirmed by reanalysis or historical data, complete a corrective action report and flag the affected compounds on the final report for matrix effect.

7.9.2 Surrogates – Control limits are determined by charting LCSs and method blanks. All of the surrogates must be within these limits in order for the analysis to be in control. If not, the reason for the malfunction must be determined and reanalysis may be necessary. If historical data indicates matrix, the sample would be flagged appropriately. When the surrogates exceed either the control limits, a corrective action report must be completed. *Federal Register* Method 624 contains no criteria for surrogate recovery.

Surrogate	**WATER**	**SOIL/SEDIMENT**
Dibromofluoromethane	85-120	80-120
1,2-Dichloroethane-d4	85-130	75-140
Toluene-d8	85-115	80-120
Bromofluorobenzene	80-120	80-125

7.9.3 Analyte concentration must be within the range of the calibration curve after rounding to 2 significant figures. If an analyte exceeds the curve, a dilution must be performed, the next sample must be checked for carryover and the sparge position must be checked for contamination through the analysis of a system blank. Any dilution should keep the concentration of the analyte in question within the mid-range of the curve.

7.9.4 Qualitative identification is made as indicated below.

7.9.4.1 The mass spectra are compared to reference spectra in a user-created data base especially compiled to contain relatively uncontaminated mass spectra of each target compound. Note: Such a file cannot be obtained from the daily calibrations during each 12 hour analytical period due to overlapping peaks in the mixes.

7.9.4.2 The GC/MS analyst uses intelligence guided by experience to make the identifications.In uncontaminated spectra where ions are missing due to low concentration, if the major ions are present in the correct ratios at the correct retention time, the identification will be considered positive. In contaminated spectra, special emphasis will be placed upon higher mass ions, and the major ions will usually need to be present as major components of the spectrum (either unsubtracted or subtracted) for the identification to be positive. All assessments of relative intensities of ions will be made by visual estimates from the spectra.

7.10 Calculations:

7.10.1 The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.

A_{is} = Peak area (or height) of the internal standard.

C_s = Concentration of the analyte or surrogate.

C_{is} = Concentration of the internal standard.

7.10.2 Calibration verification involves the calculation of the percent drift (linear) or the percent difference (average) of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference, depending on the calibration procedure used.

$$\% \text{ Drift} = \frac{(\text{Calculated concentration} - \text{Theoretical concentration}) * 100}{\text{Theoretical Concentration}}$$

where the calculated concentration is determined from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{(\text{CCV RF} - \text{Average RF}) * 100}{\text{Average RF}}$$

where CCV RF is the response factor from the analysis of the verification standard and Average RF is the average response factor from the initial calibration. The % difference or % drift calculated for the calibration verification standard must be within ±20% for each CCC analyte, or for all target analytes if the CCCs are not target analytes, before any sample analyses may take place.

7.10.3 Concentration in water samples is calculated as follows: [Note: Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to ug/L.]

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(V_s)(1000)}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

A_{is} = Area (or height) of the peak for the internal standard.

C_{is} = Concentration of the internal standard in the volume purged in ug/L.

D = Dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

V_i = For purge-and-trap analysis, V_i is not applicable and is set at 1.

$\overline{RF}$ = Mean response factor from the initial calibration.

V_s = Volume of the aqueous sample purged (mL). If units of liters are used for this term, multiply the results by 1000.

7.10.4 Concentration in non-aqueous samples is calculated as follows: [Note: Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to ug/kg.]

$$\text{Concentration } (\mu\text{g/kg}) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(W_s)(1000)}$$

where: A_s,

A_{is}, C_{is}, D, and $\overline{RF}$ are the same as for aqueous samples, and

W_s = Weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

8.0 QUALITY ASSURANCE/QUALITY CONTROL/CORRECTIVE ACTIONS

8.1 Internals - All samples and QC are spiked with internals. See section 7.9.1 above for criteria and corrective action.

8.2 Surrogates - All samples and QC are spiked with surrogates. The surrogate recoveries from method blanks and LCS are used to generate control limits. See section 7.9.2 above for criteria and corrective action.

8.3 LCS Sample - An LCS is analyzed every 12 hour tune. To prepare the LCS, a blank is spiked with standards prepared from an alternate vendor or lot number from the calibration standards. Note: the concentration of the LCS will be 20 µg/L when analyzing 624 samples (QC Check Sample). The recoveries are used to generate control limits. See the LCS report forms in the appendix for the laboratory generated limits. The limits are in-house generated matrix spike limits or client specified limits for matrix spike analytes and 70-130% (or client specified limits) recovery for waters or soils for all other analytes if limits have not been generated. Limits for 624 LCSs are taken from table 5 of method 624. If the LCS compound has a recovery above the upper limit, but the same compound is not detected in any of the batch samples, no corrective action is required. For all other situations, the LCS should be reanalyzed for the failed analytes only. If the second analysis fails, all associated samples should be reanalyzed for the failed analytes only.

8.4 Method Blanks - The concentration for most method target analytes must be < ½ the reporting limit. Common laboratory contaminants, such as acetone and

methylene chloride, must be < the reporting limit. The first step of corrective action is to assess the affect on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps should be taken to find/reduce/eliminate the source of this contamination in the method blank. If an analyte is found in the method blank and some, or all, of the other batch samples, then corrective action is required. The source of contamination must be investigated and appropriate action taken and documented to find/reduce/eliminate the source of this contamination. The method blank, and any samples containing the same contaminant, would likely be reanalyzed. For the common laboratory contaminants, meeting the above requirements is not practical. Random cases of contamination are difficult to control, however, daily contamination is not acceptable and corrective action is essential. If a contaminant is found in the method blank and the samples, the compound concentration must be flagged with a 'B' on the final report unless the concentration is greater than 10x that found in the method blank. A method blank is analyzed every 12 hour tune.

8.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample - 1 in 20 samples are spiked for an MS/MSD with the LCS standard. Criteria for the MS/MSD recoveries are the same as the LCS limits. Limits for the RPDs are found on the forms in the appendix. Samples that do not meet these criteria due to matrix must be flagged on the final report for QC problems. Generally, batch control is not based on MS/MSD results unless general method failure is determined to be the problem. In that case, the samples and associated QC would be reanalyzed for the failed analytes only. MS data evaluation must include the consideration of the following factors.

8.5.1 Sample matrix - If the sample is a soil, grab sample or sequentially collected water sample it may affect the %R and RPD of the MS/MSD. A water sample which was taken from the same VOA vial for the original sample and the MS/MSD should have very good RPDs unless there has been a method problem. Corrective action must be taken in the form of reanalysis if a method problem is indicated.

8.5.2 Original sample concentration - If a spiked compound has a problem and the concentration of that compound in the original sample was two or more times the concentration of the spike, no further corrective action may be necessary other than the generation of a corrective action report to document the problem.

8.5.3 MS vs. MSD - If a spiked compound has a problem in both the MS and MSD, review the LCS and if acceptable no further action may be necessary since it is attributable to matrix effect.

8.5.4 Non-target Interference - The presence of significant non-target interference should be brought to the immediate attention of your supervisor who should discuss the problem with the client/project manager to determine the action to be taken.

9.0 HEALTH AND SAFETY

9.1 Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of blue nitrile gloves and lab coats is highly recommended.

9.2 Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples that need special consideration have applicable notes on the sample logs.

9.3 MSDS sheets are available for all reagents and standards that have been purchased. These are located in the office next to the technical director.

10. WASTE MANAGEMENT AND POLLUTION PREVENTION

10.1 Please see Waste Disposal, SOP-210 and SOP-405 for proper disposal of waste coming from this area within our laboratory.

10.2 Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

11.0 EXAMPLE FORMS

Definitions and examples of the instrument run log, LCS report sheets (624, water and soil) and the USACE analyst data review checklist are located in the following Appendix.

APPENDIX

TABLE OF DEFINITIONS

1. amu- atomic mass unit
2. BFB- Bromofluorobenzene
3. °C- degrees Centigrade
4. CCC- Calibration Check Compound
5. CCV- Continuing Calibration Verification
6. CLP- Contract Laboratory Program
7. %D- percent difference
8. EICP- extracted ion current profile
9. EPA- Environmental Protection Agency
10. g- gram or grams
11. GC- Gas Chromatograph
12. GC/MS- Gas Chromatograph/Mass Spectrometer
13. ICV- Initial Calibration Verification
14. I.D.- inner diameter
15. ISTD- internal standard
16. LSC- Laboratory Sample Concentrator
17. MDL- method detection limit
18. MS- Matrix Spike
19. MSD- Matrix Spike Duplicate
20. M.S.- Mass Spectrometer
21. µm- micometer
22. µL- microliter
23. mL- milliliter
24. mm- millimeter
25. ng- nanogram
26. P&T- purge and trap
27. QC- quality control
28. %R- percent recovery
29. RPD- relative percent difference
30. %RSD- percent relative standard deviation
31. SOP- Standard Operating Procedure
32. Surr.- surrogate
33. SPCC- System Performance Check Compound
34. TCLP- Toxicity Characteristic Leaching Procedure
35. USACE- United States Army Corps Of Engineers
36. VOA- volatile organic analysis
37. LCS- Lab Control Sample

REFERENCES

1. *40 CFR, Part 136*; Appendix A
2. *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition
3. *National Environmental Laboratory Accreditation Conference*; CH. 5, 2001
4. USACE, *EM 200-1-3; Appendix 1; Shell*, 2/2001
5. *DOD Quality Systems Manual for Environmental Laboratories*, 6/2002

FORM 3

WATER VOLATILE LAB CONTROL SAMPLE (624)

Lab Name: Empirical Laboratories, LLC Contract: ELAB

Lab Code: NA Batch No.: NA SAS No.: NA SDG No.:

Matrix Spike - Client Sample No.:

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	LCS CONCENTRATION (ug/L)	LCS % REC #	QC. LIMITS REC.
Acrolein	100.00	0.0000	100.000	100	NML
Acrylonitrile	100.00	0.0000	100.000	100	NML
Benzene	20.00	0.0000	20.000	100	64-136
Bromodichloromethane	20.00	0.0000	20.000	100	66-134
Bromoform	20.00	0.0000	20.000	100	71-129
Bromomethane	20.00	0.0000	20.000	100	14-186
Carbon tetrachloride	20.00	0.0000	20.000	100	73-127
Chlorobenzene	20.00	0.0000	20.000	100	66-134
Chloroethane	20.00	0.0000	20.000	100	38-162
2-Chloroethyl vinyl eth	40.00	0.0000	40.000	100	D-224
Chloroform	20.00	0.0000	20.000	100	68-132
Chloromethane	20.00	0.0000	20.000	100	D-204
Dibromochloromethane	20.00	0.0000	20.000	100	68-132
1,2-Dichlorobenzene	20.00	0.0000	20.000	100	63-137
1,3-Dichlorobenzene	20.00	0.0000	20.000	100	73-127
1,4-Dichlorobenzene	20.00	0.0000	20.000	100	63-137
1,1-Dichloroethane	20.00	0.0000	20.000	100	73-127
1,2-Dichloroethane	20.00	0.0000	20.000	100	68-132
1,1-Dichloroethene	20.00	0.0000	20.000	100	51-149
trans-1,2-Dichloroethen	20.00	0.0000	20.000	100	70-130
1,2-Dichloropropane	20.00	0.0000	20.000	100	34-166
cis-1,3-Dichloropropene	20.00	0.0000	20.000	100	24-176
trans-1,3-Dichloroprope	20.00	0.0000	20.000	100	50-150
Ethylbenzene	20.00	0.0000	20.000	100	59-141
Methylene chloride	20.00	0.0000	20.000	100	61-139
1,1,2,2-Tetrachloroetha	20.00	0.0000	20.000	100	61-139
Tetrachloroethene	20.00	0.0000	20.000	100	74-126
Toluene	20.00	0.0000	20.000	100	75-125
1,1,1-Trichloroethane	20.00	0.0000	20.000	100	75-125
1,1,2-Trichloroethane	20.00	0.0000	20.000	100	71-129
Trichloroethene	20.00	0.0000	20.000	100	67-133
Trichlorofluoromethane	20.00	0.0000	20.000	100	48-152
Vinyl chloride	20.00	0.0000	20.000	100	4-196

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

NML = No Method Limits

COMMENTS: _____

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VOA Water Limits

	Water	DOD Limits		Final
1,1,1 Trichloroethane	80-130	65-130		80-130
1,1,1,2-Tetrachlorethane	85-120	80-130		85-120
1,1,2,2-Tetrachloroethane	55-140	65-130		65-130
1,1,2-Trichloroethane	80-120	75-125		80-120
1,1-Dichloroethane	80-125	70-135		80-125
1,1-Dichloroethene	65-120	70-130		70-130
1,2,4 Trichlorobenzene	60-125	65-135		65-135
1,2-Dibromo-3-chloropropane	65-125	50-130		65-125
1,2-Dibromoethane	85-115	80-120		85-115
1,2-Dichlorobenzene	85-110	70-120		85-110
1,2-Dichloroethane	75-130	70-130		75-130
1,2-Dichloropropane	80-120	75-125		80-120
1,3-Dichlorobenzene	80-110	75-125		80-110
1,4-Dichlorobenzene	80-110	75-125		80-110
2-Butanone	65-140	30-150		65-140
2-Hexanone	75-140	55-130		75-140
4-Methyl-2-pentanone	75-135	60-135		75-135
Acetone	65-155	40-140		70-130
Benzene	75-120	80-120		80-120
Bromochloromethane	85-120	65-130		85-120
Bromodichloromethane	85-140	75-130		85-140
Bromoform	70-130	70-130		70-130
Bromomethane	50-160	30-145		50-160
Carbon disulfide	65-145	35-160		65-145
Carbon tetrachloride	75-135	65-140		75-135
Chlorobenzene	80-110	80-120		80-110
Chloroethane	60-145	60-135		60-145
Chloroform	80-125	65-135		80-125
Chloromethane	35-160	40-125		40-125
Cis-1,2-Dichloroethene	75-125	70-125		75-125
Cis-1,3-Dichloropropene	80-125	70-130		80-125
Dibromochloromethane	80-120	60-135		80-120
Dibromomethane	90-120	75-125		75-125
Dichlorodifluoromethane	10-180	30-155		30-155
Ethylbenzene	80-120	75-125		80-120
Methylene chloride	65-135	55-140		70-130
M,p-Xylene	80-120	75-130		80-120
o-Xylene	80-120	80-120		80-120
Styrene	80-120	65-135		80-120
Tetrachloroethene	75-115	45-150		75-115
Toluene	75-115	75-120		75-115
Trans-1-2 Dichlorethene	75-125	60-140		75-125
Trans-1-3-Dichloropropene	75-115	55-140		75-115
Trichloroethene	75-120	70-125		75-120
Trichloroflurormethane	70-140	60-145		70-140
Vinyl chloride	40-150	50-145		50-145

VOA Soil Limits

	Soil	DOD Limits		Final
1-1-1-2 Tetrachloroethane	75-130	75-125		75-130
1-1-1-Trichloroethane	75-130	70-135		75-130
1-1-2-2-Tetrachloroethane	65-130	55-130		65-130
1-1-2-Trichloroethane	70-130	60-125		70-130
1-1-Dichloroethane	75-130	75-125		75-130
1-1-Dichloroethene	65-115	65-135		65-115
1-2-4-Trichlorobenzene	65-125	65-130		65-125
1-2-Dibromo-3-chloropropane	60-135	40-135		60-135
1-2-Dibromoethane	75-125	70-125		75-125
1-2-Dichlorobenzene	75-120	75-120		75-120
1-2-Dichloroethane	75-135	70-135		75-135
1-2-Dichloropropane	75-120	70-120		75-120
1-3-Dichlorobenzene	70-120	70-125		70-120
1-4-Dichlorobenzene	60-135	70-125		70-125
2-Butanone	60-145	30-160		60-145
2-Hexanone	60-140	45-145		60-140
4-Methyl-2-pentanone	70-135	45-145		70-135
Acetone	30-180	20-160		70-130
Benzene	75-115	75-125		75-115
Bromochloromethane	80-120	70-125		80-120
Bromodichloromethane	85-140	70-130		85-140
Bromoform	70-125	55-135		70-125
Bromomethane	45-170	30-160		45-170
Carbon disulfide	65-145	45-160		65-145
Carbon tetrachloride	75-125	65-135		75-125
Chlorobenzene	75-120	75-125		75-120
Chloroethane	55-145	40-155		55-145
Chloroform	75-125	70-125		75-125
Chloromethane	40-155	50-130		50-130
Dibromochloromethane	70-125	65-130		70-125
Dibromomethane	80-120	75-130		80-120
Dichlorodifluoromethane	15-150	35-135		35-135
Ethylbenzene	70-120	75-125		70-120
Methylene chloride	35-170	55-140		70-130
Styrene	70-120	75-125		70-120
Tetrachloroethene	65-125	65-140		65-125
Toluene	70-120	70-125		70-120
Trichloroethene	75-120	75-125		75-120
Trichlorofluoromethane	65-130	25-185		65-130
Vinyl Acetate	10-240			10-240
Vinyl chloride	40-140	60-125		60-125
cis-1-2-Dichlorethene	75-120	65-125		75-120
cis-1-3-Dichloropropene	80-130	70-125		80-130
m-p-Xylene	70-120	80-125		70-120
o-Xylene	70-120	75-125		70-120
trans-1-2-Dichloroethene	75-120	65-135		75-120
trans-1-3--Dichloropropene	65-120	65-125		65-120

VOA MIXES

LIQUID MIX (2000PPM)
C-610H (PRIMARY STANDARD)
M-502A-R-10X (ICV/LCS/MATRIX SPIKE)

Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
n-Butylbenzene
sec-Butylbenzene
tert-butylbenzene
Carbon tetrachloride
Chlorobenzene
Chloroform
2- & 4-Chlorotoluene
Trichloroethene
Dibromochloromethane
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,1- & 1,2-Dichloroethane
1,1,2-Trichloroethene
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2- & 1,3-Dichloropropane
1,2,3-Trichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethylbenzene
Hexachlorobutadiene
Isopropylbenzene
Isopropyltoluene
Methylene Chloride
Naphthalene
n-Propylbenzene
Styrene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
1,2,3-Trichlorobenzene
1,2,3-Trimethylbenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
m-,p- & o-Xylene
1,1,1-Trichloroethene

GASES MIX (2000PPM)
#30042 (PRIMARY STANDARD)
M-502B-R-10X (ICV/LCS/MATRIX SPIKE)

Bromomethane
Chloroethane
Vinyl chloride
Chloromethane
Dichlorodifluoromethane
Trichlorofluoromethane

C610H-PRIMARY STANDARD
M60310X (ICV/LCS/MATRIX SPIKE)

Acrolein (10,000PPM)
Acrylonitrile (10,000PPM)

CCS1037-PRIMARY CUSTOM MIX (5000PPM)
#557102- ICV/LCS CUSTOM MIX (5000PPM)

Tetrahydrofuran
MTBE
Methyl metacrylate
Ethyl methacrylate
1,1,2-Trichlorotrifluoroethane
Cyclohexane
Methylcyclohexane
Methyl acetate
Carbon disulfide
Iodomethane

PRIMARY and ICV/LCS STANDARD-neat

Vinyl acetate (5000PPM)

PRIMARYand ICV/LCS STANDARD-neat

2-Chloroethyl vinyl ether (20000PPM)

KETONES MIX (5000PPM)
#30006 (PRIMARY STANDARD and ICV/LCS) different lots

Acetone
2-butanone
2-hexanone
4-methyl-2-pentanone

VOA CALIBRATIONS RANGE FOR EPA8260B/624(AQUEOUS)

Liquid mix, Gases mix & primary custom mix is calibrated at these levels - 0.5ppb, 1.0ppb, 2.0ppb, 10ppb, 20ppb, 50ppb, 100ppb & 200ppb. The ketones mix, 2-chloroethyl vinyl ether & vinyl acetate are calibrated at these levels - 1.0ppb, 2.0ppb, 4.0ppb, 20ppb, 40ppb, 100ppb, 200ppb & 400ppb. Acrolein & Acrylonitrile are calibrated at these levels – 2.5ppb, 5.0ppb, 10ppb, 50ppb, 100ppb, 250ppb, 500ppb, 1000ppb.

VOA CALIBRATIONS RANGE FOR EPA8260B(SOLIDS)

Liquid mix, Gases mix & primary custom mix is calibrated at these levels – 2.0ppb, 5.0ppb, 10ppb, 20ppb, 50ppb, 100ppb & 200ppb. The ketones mix, 2-chloroethyl vinyl ether & vinyl acetate are calibrated at these levels - 2.0ppb, 10ppb, 20ppb, 40ppb, 100ppb, 200ppb & 400ppb. Acrolein & Acrylonitrile are calibrated at these levels – 5.0ppb, 10ppb, 50ppb, 100ppb, 250ppb, 500ppb, 1000ppb.

VOA LCS/ICV/MATRIX SPIKE LEVEL FOR EPA8260B

Liquid mix, Gases mix, Ethyl methacrlate, Metyl methacrylate, Tetrahydrofuran, MTBE, Trichlorotrifluoroethane, Cyclohexane, Methylcyclohexane & Methyl acetate are spiked at 50ppb level. Acrolein & Acrylonitrile spiked at 250ppb level. Acetone, 2-Butanone, 2-Hexanone, Carbon disulfide, 2-Chloroethyl vinyl ether, 4-Methyl-2-pentanone, Vinyl acetate & Iodomethane are spiked at 100ppb level.

INTERNAL STANDARD ASSOCIATION / QUANT ION TABLE

COMPOUND	QUANT MASS	* I.S.	COMPOUND	QUANT MASS	* I.S.
			Dibromomethane	93	1
*Fluorobenzene **(1)**	96		1,1,2-Trichloroethane	83	2
*Chlorobenzene-d5 **(2)**	117		1,2,3-Trichloropropane	110	2
*1,4-Dichlorobenzene-d4 **(3)**	152		Hexachlorobutadiene	225	3
			Isopropylbenzene	105	2
Bromomethane	94	1	Isopropyltoluene	119	3
Chloroethane	64	1	Methylene Chloride	84	1
Vinyl chloride	62	1	Naphthalene	128	3
Chloromethane	50	1	Propionitrile	54	1
Dichlorodifluoromethane	85	1	n-Propylbenzene	91	3
Acetonitrile	41	1	Styrene	104	2
Allyl chloride	41	1	1,1,1,2-Tetrachloroethane	131	2
Trichlorofluoromethane	101	1	1,1,2,2-Tetrachloroethane	83	3
Benzene	78	1	Tetrachloroethene	166	2
Bromobenzene	156	3	Toluene	92	2
Bromochloromethane	128	1	1,2,3-Trichlorobenzene	180	3
Bromodichloromethane	83	2	1,2,4-Trichlorobenzene	180	3
Bromoform	173	2	1,2,4-Trimethylbenzene	105	3
n-Butylbenzene	91	3	1,3,5-Trimethylbenzene	105	3
sec-Butylbenzene	105	3	m-Xylene	91	2
tert-butylbenzene	119	3	p-Xylene	91	2
Carbon tetrachloride	117	1	o-Xylene	91	2
Chlorobenzene	112	2	Acrolein	56	1
Chloroform	83	1	Acrylonitrile	53	1
Chloroprene	53	1	Tetrahydrofuran	42	1
2-Chlorotoluene	91	3	MTBE	73	1
4-Chlorotoluene	91	3	Methacrylonitrile	41	1
Dibromochloromethane	129	2	Methyl methacrylate	41	1
1,2-Dibromo-3-chloropropane	157	3	Ethyl methacrylate	69	2
1,2-Dibromoethane	107	2	1,1,2-Trichlorotrifluoroethane	101	1
1,2-Dichlorobenzene	146	3	Cyclohexane	56	1
1,3-Dichlorobenzene	146	3	Methylcyclohexane	83	1
1,4-Dichlorobenzene	146	3	Methyl acetate	43	1
1,1-Dichloroethane	63	1	Carbon disulfide	76	1
1,2-Dichloroethane	62	1	Iodomethane	142	1
1,1-Dichloroethene	96	1	Vinyl acetate	43	1
cis-1,2-Dichloroethene	96	1	2-Chloroethyl vinyl ether	63	1
trans-1,2-Dichloroethene	96	1	Acetone	43	1
trans-1,4-Dichloro-2-butene	53	3	2-butanone	43	1
1,2-Dichloropropane	63	1	2-hexanone	43	2
1,3-Dichloropropane	76	2	Isobutyl alcohol	43	1
2,2-Dichloropropane	77	1	1,4-Dioxane	88	1
1,1-Dichloropropene	75	1	4-methyl-2-pentanone	43	1
cis-1,3-Dichloropropene	75	1	Dibromofluoromethane (S)	111	1
trans-1,3-Dichloropropene	75	2	1,2-Dichloroethane-d4 (S)	102	1
Ethylbenzene	91	2	Toluene-d8 (S)	98	2
1,1,1-Trichloroethane	97	1	Bromofluorobenzene (S)	95	2
Trichloroethene	95	1			

***I.S=internal Standard.**
S=surrogate.

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):	
Batch Number(s):	
Method:	**8260B/8270C (Circle One)**

QA/QC Item	Yes	No	NA	Second Level Review
1. Is the BFB/DFTPP tune performed every 12 hours and is the tuning criteria met?				
2. Are the RRFs and % RSDs within QC limits for appropriate analytes for the initial calibration? Check the retention times for compounds with the same spectra. Check compounds with different conc.(eg. m/p-xylene, ketones,etc.).				
3. Was the initial calibration curve verified by a second source calibration standard (ICV) and have criteria been met?				
4. Does the Continuing Calibration Standard (CCV) meet the criteria for the CCCs and SPCCs.				
5. Is the Method Blank run at the desired frequency and is its concentration for target analytes less than the MDLs?				
6. Are the LCS, MS, MSD within control limits and run at the desired frequency?				
7. Are all sample holding times met, analytes within calibration range, IS areas and surrogate recoveries within QC limits?				
8. Was the Method Blank, LCS, MS, MSD and samples loaded to the GCMS_LFSYS Tablespace within the Target DB Database?				

Comments on any "No" response:

Primary-Level Review: _____ Date: _____

Second-Level Review: _____ Date: _____

TOTAL ORGANIC CARBON (TOC)

SM5310C, USEPA METHOD 415.1 SW846 METHOD 9060 AND LLOYD KAHN METHOD

SOP NUMBER: **SOP-221**

REVISION NUMBER: **6**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: **05/06/08**

DATE OF LAST REVIEW: **05/06/08**

TOTAL ORGANIC CARBON (TOC)
BY SM5310C, EPA METHOD 415.1, SW846 METHOD 9060 AND Lloyd KAHN
METHOD "*DETERMINATION OF TOC IN SEDIMENT*"

I. SCOPE AND APPLICATION

This SOP describes the measurement of TOC by SM5310C, EPA Method 415.1, SW-846 Method 9060 and Lloyd Kahn Method for determination in soil /sediment matrix.

SM5310C is used to determine the concentration of organic carbon in source and drinking water, EPA Method 415.1, SW-846 Method 9060 are used to determine concentrations of carbon in saline waters, domestic and industrial wastes and SW846 Method 9060 is modified for soil determination and the L1oyd Kahn Method is used for determination of TOC in soil/sediment and solid matrices. SW846 Method 9060 and the Lloyd Kahn Method require quadruplicate analysis of samples, where as SM5310C and 415.1 only require single analysis. These methods should be read over carefully by the analyst and any restrictions should be noted.

II. SUMMARY OF METHOD

The organic carbon is measured using an Shimadzu Total Organic Carbon Analyzer (aqueous samples) and an OI Analytical Solids TOC Analyzer model 1010 (soil/sediment samples). The Shimadzu instrument converts the organic carbon in a sample using wet chemical oxidation. The CO_2 formed is then measured by an infrared detector (replaces ultraviolet detector in SM 5310C). With the model 1010 Solids TOC analyzer, TOC is determined by acidifying a sample and heating it to 250°C to remove the TIC. The sample is then heated to 900°C to combust the remaining TOC. The resulting carbon dioxide from the TOC is detected by a non-disperse infrared (NDIR) detector that has been calibrated to directly display the mass of carbon dioxide detected. This mass is proportional to the mass of TOC in the sample.

The limit of detection for the water method is 0.50 mg carbon/L and the Limit of quantitation is 1.0 mg carbon/L. The limits of detection and quantitation with the soil method depends on the how many grams of sample is used for the analysis. For a 250 mg sample the limit of detection is 460 mg/kg and the limit of quantitation is 1600 mg/kg.

III. SAMPLING HANDLING AND PRESERVATION

3.1 Sampling and storage in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples. NOTE 1: A brief study performed in the EPA Laboratory

indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

3.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. The holding time is 28 days for waters and soils with the exception of the Lloyd Kahn method soils, which requires a 14 day holding time. Also, samples must be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

3.3 When water samples cannot be analyzed immediately, the sample is preserved by acidification to (pH </= 2) with HCl or H_2SO_4. Both water and soil samples are stored at 4°C.

IV. INTERFERENCES

4.1 WATER METHOD

4.1.1 Removal or carbonate and bicarbonate carbon by acidification and purging with purified gas results in the loss of volatile organic substances. The volatiles also can be lost during sample blending, particularly if the temperature is allowed to rise. Another important loss can occur if large carbon-containing particles fail to enter the needle used for injection. Filtration although necessary to eliminate particulate organic matter when only DOC is to be determined, can result in loss or gain of DOC, depending on the physical properties of the carbon-containing compounds and the adsorption of carbonaceous material on the filter, or its desorption from it. Check filters for their contribution to DOC by analyzing a filtered blank. Note that any contact with organic material may contaminate a sample. Avoid contaminated glassware, plastic containers, and rubber tubing. Analyze treatment, system, and reagent blanks.

4.1.2 This procedure is applicable only to homogenous samples which can be injected into the apparatus reproducibly by means of a pipette. The openings of the pipette limit the maximum size of particles which may be included in the sample.

4.2 SOIL METHOD

4.2.1 All materials must be routinely demonstrated to be interference –free under the analysis conditions by running blanks. Use high purity or purified reagents and gases to help minimize interference problems.

4.2.2 The infrared detector is sensitized to CO_2 and accomplishes virtually complete rejection of response from other gases that absorb energy in the infrared region.

V. DEFINITIONS

5.1 ANALYTICAL BATCH-The set of samples extracted /distilled/ or digested at the same time to a maximum of 20 samples.

5.2 CALIBRATION BLANK (CB)- A volume of reagent water in the same matrix as the calibration standards, but without the analyte.

5.3 CALIBRATION STANDARD (CAL)- A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

5.4 FIELD BLANK (FMB)- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all preanalysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

5.5 FIELD DUPLICATE (FD)- Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

5.6 LABORATORY BLANK (LRB)- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to determine if the analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

5.7 LABORATORY CONTROL SAMPLE (LCS)- A solution prepared in the laboratory by dissolving a known amount of one or more pure compounds in a known amount of reagent water. Its purpose is to assure that the results produced by the laboratory remain within the acceptable limits for precision and accuracy. (This should not be confused with a calibrating standard, it must be prepared from a source other than the same source as the calibration standards).

5.8 LABORATORY DUPLICATE (LD)- Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

5.9 QUALITY CONTROL CHECK SAMPLE (QCS)- A sample containing analytes of interest at known concentrations (true value) of analytes. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory

performance using test materials that have been prepared independently from the normal preparation process.

5.10 METHOD DETECTION LIMIT (MDL)- The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

VI. REAGENTS/STANDARDS

Store all reagents and standards according to recommendations. All standards should be stored away from light and at 4°C (± 2°C).

6.1 The laboratory reagent blank water used for TOC analysis is obtained from the Modulab Analytical water purification system in the analytical laboratory. **Boiling the water is not necessary as the method states.**

6.2 Potassium hydrogen phthalate, primary stock solution, 1000 mg/L: Dissolve 0.2128g of potassium hydrogen phthalate (primary standard grade) in 100.0 mL water.

6.3. Potassium hydrogen phthalate, standard solutions : A 100 mg/L standard is prepared by transferring 10 mL of the stock solution to a 100 mL volumetric flask and diluting to the mark with water. This solution is prepared on a daily basis.

6.4. The carbonate-bicarbonate solutions are not needed for this instrument.

6.5 Calibration Standards

1. For the water method, calibration standard is Potassium Hydrogen Phthalate. Standards are made from dilutions of the stock 1000 mg/L standard as follows:

   1.0 mg/L = 0.10 mL of 1000 mg/L -> 100 mL
   2.5 mg/L = 0.25 mL of 1000 mg/L -> 100 mL
   5.0 mg/L = 0.50 mL of 1000 mg/L -> 100 mL
   10.0 mg/L = 1.0 mL of 1000 mg/L -> 100 mL
   25.0 mg/L = 5.0 mL of 1000 mg/L -> 200 mL
   50.0 mg/L = 10.0 mL of 1000 mg/L -> 200 mL
   100 mg/L = 10.0 mL of 1000 mg/L -> 100 mL

   A low level standard curve must be run for drinking water samples with the standards made as follows:

   0.25 mg/L = 0.025 mL of 1000 mg/L -> 100 mL

0.50 mg/L = 0.050 mL of 1000 mg/L -> 100 mL
1.0 mg/L = 0.10 mL of 1000 mg/L -> 100 mL
1.5 mg/L = 0.15 mL of 1000 mg/L -> 100 mL
2.5 mg/L = 0.25 mL of 1000 mg/L -> 100 mL
5.0 mg/L = 0.50 mL of 1000 mg/L -> 100 mL
10.0 mg/L = 1.0 mL of 1000 mg/L -> 100 mL

2. The soil method the calibration standard is prepared by using an OI commercially prepared 30% carbon sucrose solution.

6.6 Laboratory Control Sample:

1. For the water method, the Laboratory Control Sample is normally made from a performance evaluation solution in which the true value is known. This solution is given a unique identifier.

2. For the soil method, the Laboratory Control Sample is made from a 30% sucrose solution which is made by weighing up 7.125 grams of EM Reagent Grade Sucrose and diluting to 10 mL with deionized water volumetrically.

6.7. Persulfate oxidation solution: This solution is made by dissolving 60g of sodium persulfate in DI water, adding 15 ml of phosphoric acid and diluting to 500 ml.

6.8 Phosphoric acid solution: Dilute 100 mL of concentrated 85% phosphoric acid in 500 mL of water. This is used for water.

6.9 Phosphoric acid solution 5%: Dilute 59 mL of concentrated 85% phosphoric acid in 1000 mL of water. This is used for soil.

VII. INSTRUMENTATION

7.1 The instrument used for the Water TOC analysis is a Shimadzu Total Carbon Analyzer. An OI 1010 soil/sediment carbon analyzer is used for soil samples.

7.2 There is a Shimadzu autosampler which will hold 68 samples.

7.3 The corresponding data for each sample is obtained from the Shimadzu software for the water samples. The soil/sediment data are printed out at the organic GC printer.

VIII. AQUEOUS SAMPLE PROCEDURE

8.1 Wearing labcoat, gloves and safety glasses, the standards and check solutions should be taken out of the refrigerator and allowed to warm to room temperature. Also, remove samples from sample storage signing them out appropriately on the internal chain of custody form. Fresh acid and oxidation solutions should be poured into the appropriate containers on the front of the instrument.

8.2 Follow the instructions for operation of the instrument in Chapter 4, section 4.3 of the Shimadzu Model TOC-VWS User Manual.

8.3 **Following is a list outlining the order in which the samples should be run.** Each sample tube should be numbered and its identity entered into the TOC log book. Note: All blanks should be acidified to pH 2 to match the matrix of the samples analyzed.

1. Water Blank
2. Water Blank
3. 1.0 ppm
4. 1.0 ppm
5. Water Blank
6. Water Blank
7. 2.5 ppm
8. 2.5 ppm
9. Water Blank
10. Water Blank
11. 5.0 ppm
12. 5.0 ppm
13. Water Blank
14. Water Blank
15. 10 ppm
16. 10 ppm
17. Water Blank
18. Water Blank
19 25 ppm
20. 25 ppm
21. Water Blank
22. Water Blank
23. 50 ppm
24. 50 ppm
25. Water Blank
26. Water Blank
27. Method blank
28. Water Blank

29. Water Blank
30. LCS + 9 samples (including any sample QC) with 2 water blanks between the LCS and each sample
31. 25 ppm
32. Water Blank
33. Water Blank
34. 10 samples (including any sample QC) with 2 water blanks between each sample
35. 25ppm

8.8 Insrument printouts are generated from the software. Normal procedure is followed for preparing reports and the data is second checked before being given to the supervisor.

IX. SOIL/SEDIMENT SAMPLE PROCEDURE

A sample is introduced into the Solid Module via a conditioned sample cup. Once the sample has been introduced the entire analysis sequence is automatic. Please reference Chapter 4 of the OI 1010 Solid Module instrument manual for instrument states and configuration when initially setting the instrument methods up.
TC Mode Instrument Settings:

Analysis Temp:900°C
Analysis Time: 6.5 minutes
Nitrogen Gas Flow: 60-100 psi (external regulator regulator)
Oxygen Gas Flow: 40-60 psi (external regulator)

This is a step by step description of a routine soil TOC analysis.

9.1 The standards and check solutions should be taken out of the refrigerator and allowed to warm to room temperature. The nitrogen and oxygen (internal regulator should be set at 50-60 psi) turned on allowing a nitrogen flow of 350-400mL/minute and an oxygen flow of 180 mL/minute (± 3 mL/minute).

NOTE: DO NOT TURN THE ANALYZER ON BEFORE TURNING THE GAS ON!

9.2 Let the gas flow through the instrument for a few minutes. The instrument should now be turned on and let to stabilize for 30 minutes.

9.3 Condition the cups (with quartz wool in them) using Diagnostics under Instrument Menu commands, (don't condition too many cups at a time since setting in contact with the air can cause contamination).

9.4 Set up the subdirectory (using the current date to ID it) under WinTOC output.

9.5 If doing an initial calibration curve use an appropriate µL syringe to make the following measurements of the sucrose standard in order to achieve the indicated concentrations. Make sure that there are no air bubbles in the syringe. Turn the syringe with the needle pointed up and vibrate the barrel and disperse any air from the syringe. To enter the calibration information on the instrument go to Instrument Cal Menu, type in the calibration standard values and save the file as the cal.. date analyzed.

µL 30% Sucrose STD	Concentration (mg)
0	0
2.0 (1:6 solution)	0.10
3.0	0.90
50	15
100	30

Note: The 1:6 solution of the 30% Sucrose standard is prepared by mixing 100µL of the 30% Sucrose standard with 500µL of water.

9.6 Enter the sequence to be analyzed as listed below:

1. CCV(CCV1+ date analyzed for ID) or Initial calibration – single analyses
2. Method Blank(MB + date analyzed for ID) – single analyses
3. LCS, 15 mg dextrose (LCS + date analyzed for ID) – single analyses
4. NY Cert – 4 replicates
5. Sample – 4 replicates
6. Sample – 4 replicates
7. Sample – 4 replicates
8. Sample – 4 replicates
9. Sample – 4 replicates
10. CCV(CCV1+ date analyzed for ID)2 – single analyses
11. Sample – 4 replicates
12. Sample – 4 replicates
13. Sample – 4 replicates
14. Sample – 4 replicates
15. Sample – 4 replicates
16. CCV (CCV2+ date analyzed for ID) – single analyses
17. Sample – 4 replicates
18. Sample – 4 replicates
19. Sample – 4 replicates
20. Sample – 4 replicates
21. Sample – 4 replicates
22. CCV(CCV3+ date analyzed for ID) – single analyses
23. Sample – 4 replicates

24. Sample – 4 replicates
25. Sample – 4 replicates
26. Sample – 4 replicates
27. Sample – 4 replicates
28. CCV(CCV4+ date analyzed for ID) – single analyses
29. SampleMS – 4 replicates
30. SampleDUP – 4 replicates
31. FCV(CCV4+ date analyzed for ID) – single analyses
32. FCB(FCB4+ date analyzed for ID) – single analyses

9.7 Samples should be stored away from light and at 4°C (± 2°C). Wearing labcoat, gloves and safety glasses remove samples from sample storage signing them out appropriately on the internal chain of custody form.

9.8 Transfer a homogeneous aliquot(~5 g) of the sample into a small pre-labeled aluminum weighing pan. Label each pan with the appropriate sample ID then add enough phosphoric acid (1-2 ml) to remove the Total inorganic carbon (TIC) when the sample is placed in an oven at 250°C. Place the samples in the 250°C oven for 10 minute and begin prepping the sample cups to weigh 0.2g-1.0g of each sample(in quadruplicate). Limit the time that the cups are exposed to the atmosphere as to reduce potential contamination. **Note: Since the samples are dried in this manner, before the sample aliquot it taken, a % solids determination and calculation is NOT necessary to report the sample concentrations in dry weight.**

9.9 Set the OI 1010 to the TC Mode and start running the sequence beginning with the initial calibration or calibration verification standard as illustrated above. Weigh each sample in quadruplicate making sure to limit the time that samples are exposed to the atmosphere.

9.10 The Excel file for calculations is located in "V:\WCM\TESTS\TOC soil\". The sample identity, its corresponding mgC reading, and the sample weight are entered into the appropriate columns. The Excel worksheet is self explanatory. Normal procedure is followed for preparing reports and the data is second checked before being given to the supervisor.

X. QC REQUIREMENTS

10.1 Analyze a laboratory control sample (LCS) for each batch of samples (maximum of 20 samples per day). If the LCS does not fall within the control limits of 80 to 120%, corrective action must be taken to find and correct the problem.

10.2 Run a method blank (PB) for each batch of samples (maximum of 20 samples per day). The PB should be less than 1/2 the reporting limit.

10.3 One matrix spike and matrix spike duplicate must be run per set of 20 samples. For water analysis, a spike and spike duplicate are made by mixing 9.85 mL of sample with 0.15 mL of 1000 mg/L standard using an ependorf pipette. The percent recoveries on a MS and a MSD should be within 75 and 125%. Relative percent difference (RPD) on duplicates should be less than 20%. If not, a corrective action (CAR) must be approved by your supervisor.

10.4 Analyze an initial calibration verification (ICV) immediately after the calibration curve. Analyze a calibration check verification (CCV) standard every tenth sample and at the end or after every fifth sample when analyzing samples in quadruplicate. Analyze a CCV after every 5th sample when analyzing soil/sediment samples. The percent recoveries should be in the range of 90 to 110%. The CCV %RSD warning limits are $\leq$15% for aqueous samples and $\leq$20% for soil/sediment samples. If the CCV % RSD exceeds 15%(aqueous) or $\leq$30% (soil/sediment) and the correlation coefficient is less than 0.990 correct the problem and re-analyze the CCV.

10.5 When analyzing water samples, all water blanks before samples and standards must be below the detection limit, otherwise the samples must be rerun.

10.6 Analyze an initial calibration blank (ICB) following the ICV. Analyze a continuing calibration blank (CCB) following each CCV. The ICB and CCB should be less than $\pm$ the MDL.

10.7 Calculate all percent recoveries and relative percent differences on duplicates and show calculations on data.

10.8 Calculate all percent recoveries and relative percent differences on duplicates and show calculations on data.

Calculate spikes as follows where everything is in concentration.

$$\% \text{ Recovery} = \frac{\text{Spike} - \text{Sample}}{\text{True Value}} \times 100$$

. Relative percent difference is calculated as follows, with everything in concentration:

$$\text{RPD} = \frac{\text{Higher Concentration} - \text{Lower Concentration}}{\text{Average of Concentrations}} \times 100$$

10.9 SM5310B and EPA Method 415.1 require a single analyses per sample but SW-846 Method 9060 requires quadruplicate analysis of each sample. The Loyd Kahn soil method suggests 1 sample per 20 be run in quadruplicate. Some clients may request that all samples to be done in quadruplicate. Please check with your supervisor if you have any questions about the required numbered of sample replications.

10.10 **For aqueous samples check an acidified 20mg/L inorganic carbon standard quarterly, to assure that purge gas flow is adequate to remove inorganic carbon. The result should be below the reported quantitation limit.**

XI. CORRECTIVE ACTIONS

11.1 INSTRUMENT RELATED

1. ICV not within ± 20% (Soil) or ± 10% (415.1)
   a. If the problem is with the solution.
      i. Re-prepare, obtain new stock if necessary.
   b. If the problem is with the calibration.
      i. Recalibrate through analysis of appropriate standards and recheck ICV.
2. CCV not within ± 30% (Soil) or ±15% (415.1)
   a. If the problem is with the solution.
      i. Re-prepare, obtain new stock if necessary.
   b. If the problem is with the calibration.
      i. Recalibrate through analysis of appropriate standards and re-prepare /reanalyze the previous ten sample according the following guidelines.
         a. If the CCV was biased high, any of the previous ten samples which were below the minimum detection limit do not require reanalysis.
         b. If the CCV was biased low, the previous ten samples must be reanalyzed.

*** Incorrectly set gas flow is a common instrument related problem which requires corrective action. Verify that all gas flows are adjusted properly.**

11.2 SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20% aqueous or ±50% soil/sediment
   i. The associated sample data must be qualified on the final report.
2. Spike analysis recovery not within ±25% aqueous or ±50% soil/sediment
   i. If the analyte level in the sample is greater than 4X the spiking level, the %recovery can not be evaluated and no action is taken.
   ii. If the analyte level in the sample is not greater than 4X the spiking level, the associated sample data must be qualified on the final report. A corrective action report must accompany the data and be emailed or given to the supervisor.

XII. HEALTH AND SAFETY

A. Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of blue nitrile gloves and lab coats is highly recommended.

B. Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples which need special consideration have applicable notes on the sample logs.

C. MSDS are available for all reagents and standards, which have been purchased. These are located in the administrative section next to the break room.

D. Please see *Waste Disposal; SOP-405* for proper disposal of the waste generated from this area.

XIII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIV. METHOD PERFORMANCE

14.1 Precision and Bias for Total Organic Carbon (TOC) by Persulfate-Ultraviolet Oxidation. (Water samples)

Characteristic Of Analysis Concentration determined, mg/L:	Spring Water	Spring Water +0.15 mg/L KHP*	Tap Water	Tap Water +10 mg/L KHP*	Municipal Wastewater Effluent
Replicate 1	0.402	0.559	2.47	11.70	5.88
Replicate 2	0.336	0.491	2.49	11.53	5.31
Replicate 3	0.340	0.505	2.47	11.70	5.21
Replicate 4	0.341	0.523	2.47	11.64	5.17
Replicate 5	0.355	0.542	2.46	11.55	5.10
Replicate 6	0.366	0.546	2.46	11.68	5.33
Replicate 7	0.361	0.548	2.42	11.55	5.35
Mean, mg/L	0.35	0.53	2.46	11.53	5.32
Std. Deviation: mg/L	0.02	0.03	0.02	0.21	0.23
%	6	6	1	2	4
Actual Value,	-	0.50	-	12.46	-

mg/L					
Recovery, %	**-**	**106**	**-**	**93**	**-**
Error, %	**-**	**6**	**-**	**7**	**-**

***KHP = potassium acid phthalate.**

14.2 There was no method performance data available for the soil procedure.

XV. REFERENCES

Annual Book of ASTM Standards, Part 31, "Water," Standard D 2574-79, p. 469 (1976).

Methods for Chemical Analysis of Water and Wastes, EPA Series Method 415.1.

Standard Methods for the Examination of Water and Wastewater, 14th ed. , p. 532, Method 505 (1975).

EPA SW-846, Method 9060.

Lloyd Kahn Method, *"Determination of Total Organic Carbon in Sediment"*

GC/MS LOW LEVEL PAH'S

BY SW846 METHOD 8270C

SOP NUMBER: **SOP-231**

REVISION NUMBER: **1**

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: **01/28/08**

DATE OF LAST REVIEW: **01/28/08**

GC/MS LOW LEVEL PAH'S BY SW846 METHOD 8270C

1.0 SCOPE AND APPLICATION

This SOP (based primarily on SW-846 Method 8000B/8270C) is used for the analysis of semi-volatile organic compounds in a variety of matrices (soils, sediments, waters, etc.). The normal laboratory list of PAH analytes with their water and soil LCS limits are found attached in the appendix. Any questions left by this SOP should be answered by reading the method SW-846 8000B/8270C. If questions still remain unanswered, check with the Organic Lab Manager, QA/QC Officer and/or Technical Director. A documentation of capability (DOC) should be performed by each analyst using this method.

2.0 METHOD SUMMARY

After sample preparation using the appropriate extraction technique, the sample is introduced into the GC/MS using direct injection. The analytes are separated in the gas chromatograph by a combination of the temperature program, the pressure program and the capillary column. The analytes are then detected by the mass spectrometer. Analytes are identified by comparing the mass spectra of known standards with the mass spectra from the sample. Analytes are quantitated relative to known standards using the internal standard method.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Section 3.0 and tables 3-1 and 3-2 of the Empirical Laboratories, LLC Quality Assurance Manual include details concerning sample preservation, containers and handling of semi-volatile samples and extracts. All water and soil samples are stored in their respective walk-in coolers at a temperature of 4°C. All extracts are stored in the Hobart in the Extraction lab at a temperature of 4°C. Water samples have a holding time of 7 days from date of sampling. Soil samples have a holding time of 14 days from date of sampling with 40 days from extraction to analysis for waters and soils. (unless otherwise specified for the project).

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

4.1 All raw data (samples & QC) must be evaluated for interferences. If contamination occurs, determine whether the source of interference is in the preparation or clean-up of the samples and take corrective action to eliminate the problem.

4.2 Contamination by carryover can occur when samples of high-concentration and low-concentration are analyzed sequentially. To reduce carryover, the sample syringe must be rinsed with solvent between injections. If an unusually high sample is detected, a solvent blank should be analyzed for cross contamination.

5.0. EQUIPMENT AND APPARATUS

5.1 HP 6890 GC complete with electronic pressure control and temperature programmable gas chromatograph suitable for splitless injection.

5.2 Column: RTX-5MS (or equivalent) 30 m x 0.25 mm I.D. x 0.25 µm film thickness fused silica capillary column or RTX-5 SIL-MS 30 m x 0.28 mm I.D. x 0.5µm film thickness.

5.3 HP 5973 mass spectrometer capable of scanning from 35 to 500 amu every second or less, using 70 volts electron energy in electron impact ionization mode. The mass spectrometer is capable of producing a mass spectrum for decafluorotriphenylphosphine, DFTPP, which meets all the tuning criteria of the EPA methods.

5.4 HP 7673C autosampler capable of reproducibility from one injection to another proven by meeting QC and calibration criteria.

5.5 HP GC/MS interface that gives acceptable calibration points at 10 ng per injection for each compound of interest and achieves acceptable tuning performance criteria.

5.6 Acquisition Software: HP Chemstation system is interfaced to the GC/MS. The system acquires and stores data throughout the chromatographic programs.

5.7 Data Processing Software: Target DB on Windows NT server data system is interfaced to the HP Chemstation. The system accepts and stores acquired data. It plots by extracted ion current profile (EICP). The system is also capable of integrating the abundances in any EICP between specified time or scan-number limits. The most recent NBS mass spectral library is installed.

6.0 REAGENTS

6.1 Methylene chloride **(Please read SOP-336 before handling this solvent in our laboratory.)** – Trace analysis grade.

6.2 Stock standards are purchased in mixtures from reputable vendors. The date they are received is noted on the label and recorded in the BNA standards log book. The date they are opened is noted on the label and recorded in the BNA standards log book along with their lot number and vendor. Each standard that is prepared is recorded in the BNA standards log book and given a sequential number. Each standards label is completed with the standard number, name, preparation date, expiration date, solvent and analyst initials. All stocks and standards are stored in the freezer at a temperature of -15°C ± 5°C from the date they are received/prepared. Standards are brought to room temperature before being used to make standards. Sonication is used if precipitation is observed after bringing to room temperature. The refrigerator and freezer temperature is monitored daily with an annually calibrated thermometer and recorded with calibration correction in the Extraction temperature/calibration logbook. Makeup of common standards is detailed below. See the BNA standards log book for makeup of other standards.

6.2.1 The Decafluorotriphenylphosphine (DFTPP) tuning standard is prepared as follows (includes benzidine, pentachlorophenol and 4,4'-DDT): Using a 10µL syringe, 10µL (GCM-150, Ultra Scientific @ 1000µg/mL, or equivalent) is injected into a 1.0mL volumetric flask containing approximately 0.900mL methylene chloride (Trace Grade) and diluted to volume with same making a

10µg/mL standard. It is stored in the freezer at -15°C ± 5°C for up to 6 months. A direct injection of 1.0µL is used to tune the instrument.

6.2.2 Calibration standards are prepared from a 50µg/mL intermediate standard at a minimum of five concentrations. Calibration standards are prepared semi-annually unless the initial calibration verification standard indicates a problem. To makeup the 50µg/mL intermediate standard inject the indicated amount of the following standards (or equivalent) into a 10mL volumetric containing approximately 1mL methylene chloride (Trace Grade) and dilute to volume with the same. After capping and inverting several times, the solution is transferred into a labeled 10ml, teflon-lined, screw-capped vial and stored in the freezer at -15°C ± 5°C for up to 12 months. See the Appendix for analytes contained in these mixes.

Standard	Conc (µg/mL)	Amount(µL)	Final Conc(µL)
PAH Mix (Vendor,Lot#)	2000	250	50
BN Surrogate (Vendor,Lot#)	5000	100	50

To makeup the calibration standards, inject the indicated amount of a 5.0µg/mL intermediate standard, made from a 10x cut of the 50 ug/ml, or the 50 ug/ml into a 2mL vial containing methylene chloride (Trace Grade) and diluted to 500ul with the same. After capping and inverting several times and adding 5ul internal standard, the standards are transferred into labeled 2ml, teflon-lined, screw-capped vials and stored in the freezer at -15°C ± 5°C for up to 6 months.

Standard	Amount of standard	Amount of 100µg/mL Internal Standard
0.1 µg/mL	10 µL of 5 µg/mL	5 µL
0.2 µg/mL	20 µL of 5 µg/mL	5 µL
0.4 µg/mL	40 µL of 5 µg/mL	5 µL
1.0 µg/mL	10 µL of 50 µg/mL	5 µL
5.0 µg/mL	50 µL of 50 µg/mL	5 µL
10.0 µg/mL	100 µL of 50 µg/mL	5 µL
20.0 µg/mL	200 µL of 50 µg/mL	5 µL
30.0 µg/mL	300 µL of 50 µg/mL	5 µL

The makeup of the 5.0µg/mL CCV standard is detailed below. Note: MS list spikes and full list spikes for LCS and/or MS/MSD are prepared from an alternate source or lot number than the calibration standards.

5.0µg/mL CCV standard: Using a 50µL syringe, 50µL of a 50µg/mL working standard is injected into a 2 ml vial containing 450µL methylene chloride (Trace Grade) to make a 5.0µg/mL standard. After capping and inverting several times, 5µL of internal standard (100µg/mL) is then added and the standard is stored in the freezer at -15°C ± 5°C for up to 1 week.

6.2.3 The Initial Calibration Verification (ICV) standard is prepared from a vendor stock standard at a concentration of 50µg/mL as detailed below.

5.0 µg/mL ICV standard: Using a 50µL syringe, 50µL (C-507, NSI Solutions @ 50µg/mL, or equivalent) is injected into a 2mL vial containing 450µL methylene chloride (Trace Grade) making a 5.0µg/mL standard. After capping

and inverting several times, 5µL of internal standard (100µg/mL) is added and the standard is stored in the freezer at -15°C ± 5°C for up to 6 months.

***For some clients an SPCC curve and CCV are analyzed along with the PAH standards to check for SPCC min. responses. See standard log for preparation of these standards.**

7.0 PROCEDURE

Prior to using SW-846 8270C (semivolatile method) the samples are prepared for chromatography using the appropriate sample preparation and clean up methods (generally SW-846 methods 3510, 3520, 3541, or 3550).

7.1 Chromatographic conditions:

7.1.1 GC

Capillary Column	RTX-5MS 0.25 mm ID
Inlet mode	Pulsed Splitless
Pressure	10.81 psi (on)
Pulse Pressure	20 psi
Pulse time	2.0 minutes
Purge flow	60 mL/min.
Purge time	0.1 minute
Injector temperature	300°C
Transfer line temperature	280°C
Initial column temperature	50°C for 2.0 minutes
Initial column temperature ramp	10°C/min
Final column temperature	320°C for 3.0 minutes

7.1.2 MS

Electron energy	70 volts (nominal)
Mass range	35 to 500 amu
A/D Samples	3
Solvent Delay	4 minutes or as needed

7.2 Tuning - Prior to any calibration or analysis, DFTPP tuning criteria must be met for a 1.0µL injection of the tuning standard [see below]. Tune must be met every 12 hours sample analysis is to be performed.

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

7.3 Calibration

7.3.1 Initial Calibration - An initial calibration curve at no less than five concentration levels must be analyzed and shown to meet the initial calibration criteria before any sample analysis may be performed. Method 8270C requires that the %RSD be less than 15% to use the average response factor for quantitation, the curve is to be used otherwise as long as the correlation factor is $\geq$0.99. The lowest standard must be less than or equal to the reported quantitation limit and the highest standard must not exceed the linear range of the detector. Generally, levels for the curve are 0.1 µg/mL, 0.2 µg/mL, 0.4 µg/mL, 1.0 µg/mL, 5.0 µg/mL, 10.0 µg/mL, 20.0 µg/mL, and 30.0 µg/mL. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram. All integrations are checked for acceptability. Response factors of less than 0.050 must be supported by the mass spectrum of the lowest standard.

7.3.2 Initial Calibration Verification (ICV) - A second source standard at the 5.0 µg/mL level is used to check the validity of the curve. The standard recovery for all analytes must be between 75 and 125%. If the second source recovery is above 125%, it is possible that the main standard has deteriorated for that compound. That standard should be remade and reevaluated. If that does not correct the problem, the standard should probably be replaced and a new curve generated. If the second source recovery is below 75%, the second source standard may have deteriorated for that compound. The standard should be remade and reanalyzed. If this does not correct the problem, the standard should probably be replaced. If any compound in the ICV exceeds the criteria above, it may be evaluated and initialed by the organic section manager. If deemed acceptable, the analyst may continue analysis. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram. All integrations are checked for acceptability.

7.3.2 Continuing Calibration Verification (CCV)- Every 12 hours a CCV at 5.0 µg/mL must be analyzed and calculated against the initial calibration curve, then shown to meet the calibration criteria before any sample analysis may be performed. Acceptance criteria for 8270C analytes must be less than or equal to 20% difference or drift (%D, calculations follow in section 7.9). Internal standard areas should be within 50 to 200 percent of the area of the curve midpoint or the previous CCV. Retention times for the internal standards should be within 30 seconds of the retention time of the curve midpoint or the previous CCV. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram. All integrations are checked for acceptability. Samples are then quantitated against the initial calibration curve.

7.4 LCS - The LCS is extracted 1 per extraction batch of up to 20 samples. The LCS is spiked using an alternate source or lot number than the calibration standards. See

the LCS report forms in the appendix for the laboratory generated limits. Recoveries for the MS/MSD spike analytes in LCSs are charted annually to generate control limits for samples analyzed by method 8270C. In all cases, the lowest upper limit would be 110% and the lowest lower limit would be 10%. If enough data points are not present to generate limits, the limits default to 10-110% for all other analytes. See Section 8.3 below for corrective action.

7.5 Method Blank - Method blanks are extracted at a minimum of 1 per extraction batch - up to 20 samples. See Section 8.4 below for criteria and corrective action.

7.6 Samples - Prior to analysis, 0.5 mL samples are prepared by verifying volume and spiking with 5uL of the internal standard solution.

7.7 Data Reduction/Evaluation - Each sample analysis sequence is documented using the computer run log generated on the chemstation. This run log is signed, dated and paginated then placed in a 3 ring binder for that instrument. After the sample has been analyzed, the data is processed through Target DB on the Windows NT data system. The following must be checked to determine if the sample will need any reanalysis or dilution. Formal data evaluation is detailed in SOP-200 and documented using the Analyst Data Review Checklist (see Appendix).

7.7.1 Internal Standards - Areas should be within 50 to 200 percent of the area of the curve midpoint. Retention time should be within 30 seconds of the retention time of the curve midpoint. If not, the sample and historical data should be evaluated to determine the cause of the problem. If matrix effect is confirmed by reextraction/reanalysis or historical data, complete a corrective action report and flag the affected compounds on the final report for matrix effect. Note: criteria applies to the continuing calibration, not samples, but is used as an indication of the sample analysis validity.

7.7.2 Surrogates – Control limits are determined annually by charting LCSs and method blanks. In all cases, the lowest upper limit would be 110% and the lowest lower limit would be 10%. All of the three surrogates for each fraction must be within the control limits in order for the extraction batch to be in control. If a surrogate exceeds the limits, the reason for the malfunction must be determined and a corrective action report must be completed. The sample must be reanalyzed, reextracted or flagged for QC problems.

Surrogate	**Water**	**Soil/Sediment**
Nitrobenzene-d5	40-110	35-100
2-Fluorobiphenyl	50-110	45-105
Terphenyl-d14	50-135	30-125

7.7.3 Analyte concentration must be within the range of the calibration curve after rounding to 2 significant figures. If an analyte exceeds the curve, a dilution must be performed and the next sample must be checked for carryover. Any

dilution should keep the concentration of the analyte in question within the top half of the curve.

7.7.4 The qualitative identification of compounds is based on retention time and a comparison of the sample mass spectrum, after background subtraction, with characteristic ions in a reference mass spectrum from the NBS database (NBS75K.I). This database is used as it contains relatively uncontaminated mass spectra of each target compound which cannot be obtained from the daily calibrations during each 12 hour analytical period due to overlapping peaks in the mixes. Characteristic ions from the reference mass spectrum library are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. In addition, the following criteria must be met. The RRT of the sample analyte must be within 0.06 RRT units of the RRT of the standard analyte. The relative intensities of the characteristic ions must agree within 30% of the relative intensities of the same ions in the reference spectrum. Structural isomers that produce very similar mass spectra should be identified as individual isomers so long as their GC retention times differ substantially. A library search may be made for analytes not associated with the calibration for the purpose of tentative identification. NOTE: The GC/MS analyst uses intelligence guided by experience to make the identifications. In uncontaminated spectra where ions are missing due to low concentration, if the major ions are present in the correct ratios at the correct retention time, the identification will be considered positive. In contaminated spectra, special emphasis will be placed upon higher mass ions, and the major ions will usually need to be present as major components of the spectrum (either unsubtracted or subtracted) for the identification to be positive. All assessments of relative intensities of ions will be made by visual estimates from the spectra.

7.8 Quantitation - Once a compound has been identified qualitatively, the concentration must then be quantitated. If the RSD of the compound's response factor is 15% or less, then the concentration may be determined using the average response factor ($\overline{RF}$) from the initial calibration data. Otherwise, the concentration must be determined from equations based on internal standard calibration using either linear or non-linear calibration. Calculations follow in Section 7.9.

7.9 Calculations:

7.9.1 The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.

A_{is} = Peak area (or height) of the internal standard.

C_s = Concentration of the analyte or surrogate.

C_{is} = Concentration of the internal standard.

7.9.2 Calibration verification involves the calculation of the percent drift (linear or quadratic) or the percent difference (average) of the instrument response between the initial calibration and each subsequent analysis of the

verification standard. Use the equations below to calculate % Drift or % Difference, depending on the calibration procedure used.

$$\% \text{ Drift} = \frac{(\text{Calculated concentration} - \text{Theoretical concentration}) * 100}{\text{Theoretical Concentration}}$$

where the calculated concentration is determined from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{(\text{CCV RF} - \text{Average RF}) * 100}{\text{Average RF}}$$

where CCV RF is the response factor from the analysis of the verification standard and Average RF is the average response factor from the initial calibration. The % difference or % drift calculated for the calibration verification standard must be within ±20% for each analyte before any sample analyses may take place.

7.9.3 Concentration in water samples is calculated as follows: [Note: Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.]

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(V_s)(1000)}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

A_{is} = Area (or height) of the peak for the internal standard.

C_{is} = Concentration of the internal standard in the volume extracted in ug/L.

D = Dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

V_i = Volume of the extract injected (µL). The nominal injection volume for samples and calibration standards must be the same.

$\overline{RF}$ = Mean response factor from the initial calibration.

V_s = Volume of the aqueous sample extracted (mL). If units of liters are used for this term, multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL. If the injection (V_i) is expressed in mL, then the 1000 may be omitted.

7.9.4 Concentration in non-aqueous samples is calculated as follows: [Note: Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.]

7.9.5

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(W_s)(1000)}$$

where: A_s, A_{is}, C_{is}, D, and $\overline{RF}$ are the same as for aqueous samples, and

W_s = Weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL. If the injection (V_i) is expressed in mL, then the 1000 may be omitted.

8.0 QUALITY ASSURANCE/QUALITY CONTROL/CORRECTIVE ACTIONS

8.1 Internals - All samples and QC are spiked with internal standards. See section 7.7.1 above for criteria and corrective action.

8.2 Surrogates - All samples and QC are spiked with surrogates. The surrogate recoveries from method blanks and LCS are used to generate control control limits for the surrogates. See section 7.7.2 above for criteria and corrective action. If any surrogate recoveries are below 10%, samples must be re-extracted if sample is available.

8.3 LCS Sample - The LCS is extracted 1 per extraction batch of up to 20 samples. The LCS is spiked using an alternate source or lot number than the calibration standards. If the LCS compound has a recovery above the upper limit, but the same compound is not detected in any of the batch samples, no corrective action is required. For all other situations, the LCS should be reanalyzed for the failed analytes only. If the second analysis fails, all associated samples should be reextracted/reanalyzed for the failed analytes only or the data must be evaluated for flagging due to QC problems.

8.4 Method Blanks - The concentration of all method target analytes should be below the MDL for each method target analyte(**< ½ RL for DOD QSM**). The first step of corrective action is to assess the effect on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps should be taken to find/reduce/eliminate the source of this contamination in the method blank. If an analyte is found in the method blank and some, or all, of the other batch samples, then corrective action is required. The source of contamination must be investigated and appropriate action taken and documented to find/reduce/eliminate the source of this contamination. The method blank, and any samples containing the same contaminant, may need to be reextracted/reanalyzed. For the common laboratory contaminants, meeting the above requirements is not practical. Random cases of contamination are difficult to control, however, daily contamination is not acceptable and corrective action is essential. If a contaminant is found in the method blank and the samples, the compound concentration must be flagged with a 'B' on the final report unless the concentration is greater than 10x that found in the method blank.

8.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample - 1 in 20 samples are spiked for a MS/MSD (for full list spikes, the full list spiking solution is used). Control limits for the MS/MSD recoveries are the same as those for the LCS found in the appendix. RPD limits are found on the LCS report forms in the appendix. Samples which do not meet these criteria due to matrix must be evaluated for flagging on the final report due to QC problems. Generally, batch control is not based on MS/MSD results unless general method failure is determined to be the problem. In that case, the samples and associated QC would be reanalyzed for the failed analytes only. MS data evaluation must include the consideration of the following factors.

8.5.1 Sample matrix - If the sample is a soil, grab sample or sequentially collected water sample it may affect the %R and RPD of the MS/MSD. Corrective action must be taken in the form of reanalysis if a method problem is indicated.

8.5.2 Original sample concentration - If a spiked compound has a problem and the concentration of that compound in the original sample was two or more times the concentration of the spike, no further corrective action may be necessary other than the generation of a corrective action report to document the problem.

8.5.3 MS vs. MSD - If a spiked compound has a similar problem in both the MS and MSD and is not traced to a method problem, no further action may be necessary other than the generation of a corrective action report to document the problem.

8.5.4 Non-target Interference - The presence of significant non-target interference should be brought to the immediate attention of your supervisor who should discuss the problem with the client/project manager to determine the action to be taken.

9.0 HEALTH AND SAFETY

9.1 Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of gloves and lab coats is highly recommended.

9.2 Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples which need special consideration have applicable notes on the sample logs.

9.3 MSDS sheets are available for all reagents and standards which have been purchased. These are located on the bookshelf outside the office supply storage room.

REFERENCES

1. *Test Methods for Evaluating Solid Waste*, SW-846,Method 8270C, Third Edition.
2. *DOD Quality Systems Manual for Environmental Laboratories*, 6/2002.

10.0 EXAMPLE FORMS

Definitions and examples of the LCS report sheets (625 water limits, in-house water limits and in-house soil limits), the analyst data review checklist and figure 13 from *Federal Register* method 625 for the tailing factor calculation are located in the appendix.

APPENDIX

TABLE OF DEFINITIONS

1. amu- atomic mass unit
2. PAH-Polyaromatic hydrocarbons
3. BNA-base neutral acid
4. °C- degrees Centigrade
5. CCC- Calibration Check Compound
6. CCV- Continuing Calibration Verification
7. CLP- Contract Laboratory Program
8. %D- percent difference
9. DFTPP- Difluorotriphenyphosphine
10. EICP- extracted ion current profile
11. EPA- Environmental Protection Agency
12. g- gram or grams
13. GC- Gas Chromatograph
14. GC/MS- Gas Chromatograph/Mass Spectrometer
15. ICV- Initial Calibration Verification
16. I.D.- inner diameter
17. ISTD- internal standard
18. LSC- Laboratory Sample Concentrator
19. MDL- method detection limit
20. MS- Matrix Spike
21. MSD- Matrix Spike Duplicate
22. M.S.- Mass Spectrometer
23. µm- micometer
24. µL- microliter
25. mL- milliliter
26. mm- millimeter
27. ng- nanogram
28. NPDES- National Pollutant Discharge Elimination System
29. P&T- purge and trap
30. QC- quality control
31. %R- percent recovery
32. RPD- relative percent difference
33. RRT- relative retention time
34. %RSD- percent relative standard deviation
35. SOP- Standard Operating Procedure
36. Surr.- surrogate
37. SPCC- System Performance Check Compound
38. TCLP- Toxicity Characteristic Leaching Procedure
39. USACE- United States Army Corps Of Engineers

FORM 3

WATER PAH LAB CONTROL SAMPLE (8270C)

Lab Name: ELAB Contract:

Lab Code: NA Batch No.: NA SAS No.: NA SDG No.:

Matrix Spike - Client Sample No.:

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	LCS CONCENTRATION (ug/L)	LCS % REC #	QC. LIMITS REC.
Acenaphthene	1.00	0.0000	1.00	100	41-132
Acenaphthylene	1.00	0.0000	1.00	100	43-140
Anthracene	1.00	0.0000	1.00	100	50-139
Benzo(a)anthracene	1.00	0.0000	1.00	100	58-141
Benzo(b)fluoranthene	1.00	0.0000	1.00	100	42-156
Benzo(k)fluoranthene	1.00	0.0000	1.00	100	49-165
Benzo(g,h,i)perylene	1.00	0.0000	1.00	100	12-171
Benzo(a)pyrene	1.00	0.0000	1.00	100	31-142
Chrysene	1.00	0.0000	1.00	100	51-155
Dibenz(a,h)anthracene	1.00	0.0000	1.00	100	28-153
Fluoranthene	1.00	0.0000	1.00	100	47-158
Fluorene	1.00	0.0000	1.00	100	40-140
Indeno(1,2,3-cd)pyrene	1.00	0.0000	1.00	100	20-167
Naphthalene	1.00	0.0000	1.00	100	39-125
Phenanthrene	1.00	0.0000	1.00	100	46-144
Pyrene	1.00	0.0000	1.00	100	39-158
2-Methylnaphthalene	1.00	0.0000	1.00	100	36-121
1-Methylnaphthalene	1.00	0.0000	1.00	100	35-131

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

COMMENTS: _____

page 1 of 1

FORM III SV
FORM 3

SOIL PAH LAB CONTROL SAMPLE (8270C)

Lab Name: ELAB Contract:

Lab Code: NA Batch No.: NA SAS No.: NA SDG No.:

Matrix Spike - Client Sample No.:

COMPOUND	SPIKE ADDED (ug/Kg)	SAMPLE CONCENTRATION (ug/Kg)	LCS CONCENTRATION (ug/Kg)	LCS % REC #	QC. LIMITS REC.
Acenaphthene	67.00	0.0000	67.00	100	28-110
Acenaphthylene	67.00	0.0000	67.00	100	23-126
Anthracene	67.00	0.0000	67.00	100	28-136
Benzo(a)anthracene	67.00	0.0000	67.00	100	31.146
Benzo(b)fluoranthene	67.00	0.0000	67.00	100	30-139
Benzo(k)fluoranthene	67.00	0.0000	67.00	100	42-129
Benzo(g,h,i)perylene	67.00	0.0000	67.00	100	21-149
Benzo(a)pyrene	67.00	0.0000	67.00	100	28-128
Chrysene	67.00	0.0000	67.00	100	39-134
Dibenz(a,h)anthracene	67.00	0.0000	67.00	100	30-138
Fluoranthene	67.00	0.0000	67.00	100	30.142
Fluorene	67.00	0.0000	67.00	100	27-116
Indeno(1,2,3-cd)pyrene	67.00	0.0000	67.00	100	17-164
Naphthalene	67.00	0.0000	67.00	100	29-106
Phenanthrene	67.00	0.0000	67.00	100	32-127
Pyrene	67.00	0.0000	67.00	100	28-130
2-Methylnaphthalene	67.00	0.0000	67.00	100	30-111
1-Methylnaphthalene	67.00	0.0000	67.00	100	30-111

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

For 8270-SIM projects, the AFCEE QAPP Ver. 4.0 limits for PAHs in soil and water will be used.

PAH Mix

Acenaphthene
Acenapthylene
Anthracene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(a)pyrene
Chrysene
Dibenz(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
2-Methylnaphthalene
1-Methylnaphthalene
Naphthalene
Phenanthrene
Pyrene

BN Surrogate

2-Fluorobiphenyl
Nitrobenzene-d5
Terphenyl-d14

Internal Standards

Acenaphthene-d10
Chrysene-d12
1,4-Dichlorobenzene-d4
Naphthalene-d8
Perylene-d12
Phenanthrene-d10

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):	
Batch Number(s):	
Method:	**8260/8270 (Circle One)**

QA/QC Item	Yes	No	NA	Second Level Review
1. Is the BFB/DFTPP tune performed every 12 hours and is the tuning criteria met?				
2. Are the RRFs and % RSDs within QC limits for appropriate analytes for the initial calibration? Check the retention times for compounds with the same spectra. Check compounds with different conc.(eg. m/p-xylene, ketones,etc.).				
3. Was the initial calibration curve verified by a second source calibration standard (ICV) and have criteria been met?				
4. Does the Continuing Calibration Standard (CCV) meet the criteria for the CCCs and SPCCs.				
5. Is the Method Blank run at the desired frequency and is its concentration for target analytes less than the MDLs?				
6. Are the LCS, MS, MSD within control limits and run at the desired frequency?				
7. Are all sample holding times met, analytes within calibration range, IS areas and surrogate recoveries within QC limits?				
8. Was the Method Blank, LCS, MS, MSD and samples loaded to the GCMS_LFSYS Tablespace within the Target DB Database?				

Comments on any "No" response:

Primary-Level Review: _____ Date: _____

Second-Level Review: _____ Date: _____

GC/MS SEMI-VOLATILE BNA-AQUEOUS MATRIX EXTRACTION USING SW-846 METHOD 3510C FOR 8270C/625 ANALYSIS

SOP NUMBER: **SOP-300**

REVISION NUMBER: **16**

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: **05/27/08**

DATE OF LAST REVIEW: **05/27/08**

GC/MS BNA - AQUEOUS MATRIX EXTRACTION USING SW846 METHOD 3510C/8270C, 625

I. SCOPE AND APPLICATION/SUMMARY

1. This SOP describes the extraction of BNAs from water by separatory funnel extraction using SW846 Method 3510C and 625. Samples are extracted with methylene chloride and concentrated to an appropriate final volume.

II. INTERFERENCES

1. Solvents, reagents, glassware, and other sample processing apparatus can add interferences to sample analysis. Method blanks must be extracted under the same conditions as samples to demonstrate freedom from interferences.
2. Phthalate esters commonly found in plastics can interfere with the analysis. Plastics should be avoided.
3. Soap residue can degrade certain analytes such as aldrin and heptachlor. Glassware should be solvent rinsed to avoid this problem.

III. APPARATUS AND MATERIALS

- Separatory Funnel - 2-Liter with Teflon stopcock
- Beaker - 400 mL
- Drying /Chromatographic column - 20 mm I.D. x 300 mm or funnel
- Turbo-Vap evaporation tube - 200 mL tube made by Zymark to fit into Turbo-Vap evaporator
- Metal rack - capable of holding six glass evaporation tubes
- Turbo-Vap Evaporator - heated and capable of temperature control (±5°C); the bath should be vented into a hood.
- Vials - 2 mL glass amber, with Teflon-lined screw cap and 40 mL with Teflon lid.
- pH indicator paper - close range (1.0 - 2.0) and (10.0 - 12.0); wide range (1.0 - 12.0)
- Syringe - 1 mL, 500 mL
- Graduated cylinder - Glass, Class A, 1000 mL, 500 mL, and 100 mL
- Pasteur pipette - length 9" and 5-3/4"
- Pasteur pipette bulb
- Labels - Avery
- Teflon Bottles - 250 mL and 1000 mL
- Ring stand - 3 prong
- Aluminum foil - heavy duty
- 10 mL disposable pipette
- Nitrogen tank - equipped with pressure regulator

IV. REAGENTS

- Reagent Water - Reagent water is gathered in a carboy from source in the instrument lab daily. Remaining water in the carboy is dumped at the end of each day.

- Sodium Hydroxide Solution - (10N), Weigh 400 g NaOH (purchased in a plastic container from Fisher # S318-3 or equivalent) into a 1200 mL fleaker beaker and cover with reagent water. Swirl until all pellets are dissolved. This mixture gets very hot. Let stand until cool. Transfer to a 1-liter volumetric flask with several rinses of reagent water and dilute to 1 liter with reagent water. Transfer to a 1000-mL Teflon container.

- Sodium Sulfate - Granular, anhydrous, trace pure 10 - 60 mesh (purchased in plastic bulk containers from Fisher # S415-10S or equivalent) placed in Pyrex tray and heated at 400°C for a minimum of 4 hrs, removed and cooled in open air in the extraction lab, placed in a 2.5 kg glass amber jug and left at room temperature.

- Glass Wool - Silane Treated (purchased from Supelco #2-0410 or equivalent).

- Sulfuric Acid Solution - (1:1), slowly add 500 mL of H2SO4 (Baker, suitable for trace metal analysis #9673-33 or equivalent) to 500 mL of reagent water in a 1000 mL Teflon container. This mixture will get very warm. Allow to cool before use.

- Extraction Solvent - Methylene Chloride (**Please read SOP-336 before handling this solvent in our laboratory.)** (Dichloromethane - Omnisolv - suitable for spectrophotometry and gas chromatography #DX0831-1 or equivalent).

- The GC/MS operator makes up all surrogates and spikes. Verify the amount of surrogate/spike to add to the sample prior to addition. It can change if a different detection limit is required or the volume of sample being analyzed changes.

  BNA Surrogate - The base neutral and acid surrogates are normally mixed together in one solution. This solution is purchased from a reputable vendor. Use 0.5 mL of this solution per 1000 mLs of aqueous sample for surrogate amount of 100:200 ug/mL per sample. **(For low level PAHs use 1.0ml of a 1.0µg/mL BN Surrogate spiking solution.)**

  BNA Spiking Solution - The base neutral and acid spiking solutions are normally mixed together in one solution. This solution is prepared in methanol by making a dilution of stock purchased from a reputable vendor. Use 0.5 mL of this solution per 1000 mLs of aqueous sample for LCS amount of 100ppm per sample. There are two separate spiking solutions available – one solution has a more complete list of BNA compounds than the other which is called the short or matrix spike list. The long list should be used on all extractions unless your supervisor has approved the short list. The short list may be used for any 'phenol only' extractions. **(For low level PAHs use 1.0 ml of a 1.0ppm of the LLPAH spiking solution.)**

BNA TCLP Spike – 0.5 mL is added per 100-mL volume. Each matrix type must have its own TCLP spike. TCLP spike should be added after the TCLP has been filtered but prior to refrigeration. From the volume provided by Wet Chemistry, remove a 100-mL aliquot into a suitable container with a teflon lid, and spike as indicated above.

V. PROCEDURE

1. All waters have a seven-day holding time counted from the hour they are sampled. Determine the samples necessary to extract from the following sources (Note: never extract samples of unknown origin without discussion with supervisor):
   - Each day a backlog report will be provided indicating sample numbers with the respective analysis required. Line through all the extractions that have been completed and plan to do the remaining analysis within the required holding time.
   - Samples requiring RUSH turn around time may be logged in throughout the day which will require your immediate attention. Log-in personnel will generally communicate this need.
   - Check with log-in throughout the day and examine the COC (chain of custody) forms that arrive with each set of samples. If an analysis is ongoing, extra QC may be avoided by picking up those extractions on the same day.

2. Wearing lab coat, gloves and safety glasses, get samples from refrigerator. Samples must be signed out of the walk-in refrigerator. Enter the sample numbers, your initials and the date and time removed on the log provided. Inspect as to whether they are in glass amber jar and have a Teflon lid. Find out if any special dilutions need to be made for this client. Routine procedures for difficult matrices are listed below:

   SLUDGE - use only 100 mL and dilute to 1000 mL with reagent water.
   TCLP EXTRACT - use only 100 mL and dilute to 1000 mL with reagent water. A separate matrix spike of 100 mLs (which has already been spiked as explained in the BNA TCLP Spike section above) should be set up at the same time. Dilute to 1000 mL with reagent water.
   BAD MATRIX – for example a liquid that is partially sediment, see your supervisor to find out what dilution, if any should be made. **SPLP extract- use 1 liter**.
   NPDES client - a special list of compounds is required including benzidine. Method 625 requires that there be a spike every ten samples. The sample must be extracted and concentrated in the same day. A GC/MS screen is recommended; therefore this extraction should be coordinated with the GC/MS operator. 1 mL is added to the LCS and the matrix spike.
   ACID EXTRACT WITH BAD MATRIX - a cleanup step is added. Samples are taken to a high pH, extracted with 60 mLs methylene chloride one time as explained below in the BASE NEUTRAL EXTRACTION section. This extract is discarded. The samples are then taken to a low pH and extracted as an acid extraction. Acid extractions may be concentrated in the TurboVap.

3. **LOW LEVEL POLYAROMATIC HYDROCARBONS (PAHs) –** Samples require a BNA extraction. Use the Surrogate and BN spiking solutions specified. Low level PAHs are normally concentrated on the Turbo-Vap using Round-Bottom TV tubes to a final volume of 0.5 mL

4. Mark the amber glass container of each sample at the water meniscus with "white out" for later determination of sample volume. Check the pH by inverting the sample and touching the wide range pH paper to the portion that remains on the lid. Record this pH in the logbook.

5. Get out enough separatory funnels to extract the number of samples you have plus any additional spikes and a method blank. A method blank and an LCS must be processed with each set of samples. If the sample is a TCLP, blank fluid may be provided along with the extracted TCLP sample(s). Use only 100 mL and dilute to 1000 mL with reagent water. A matrix spike and a duplicate or a matrix spike duplicate must be processed for each analytical batch (up to a maximum of 20 samples). In the event that adequate sample is not provided to do an MS/MSD, an LCS duplicate should be done. Rinse separatory funnels with methylene chloride. Place an Avery label on each separatory funnel containing the following information: Lab #, Client name, Type of Analysis, Initial Volume-Final Volume, and the Lab prepbatch code. The lab batch code is defined as MMDDYYB# where #: 1 = 1st method blank of the day; 2 = 2nd method blank of the day; etc. The Method Blank and LCS label should include all lab #s in this set of samples.

6. Using the 1000-mL glass graduated cylinder marked NANO PURE WATER ONLY, measure 1000 mL of reagent water from the carboy and transfer it to a separatory funnel for the method blank and LCS. Transfer sample to separatory funnel that corresponds to the lab # on the sample bottle.

7. Verify the amount of surrogate/spike to add to the sample prior to addition. It can change if a different detection limit is required or the volume of sample being analyzed changes. Set out the surrogate/spike at least ten minutes before use to allow it to warm to room temperature.

   Generally 0.5 mL of BNA surrogate is added to each sample, spike, and blank with a syringe designated for BNA surrogate. **For low level PAHs use 1.0ml of a 1.0ppm LLPAH Surrogate spiking solution.** Someone must verify that the surrogate has been added by placing a check mark on each label as it is added.

   NOTE: Be sure to invert syringe and eliminate air bubble when obtaining surrogate solution and spiking solution.

   For the sample in each analytical batch selected for spiking, use the 0.5-mL glass syringe designated for BNA spike, to add 0.5 mL of BNA spiking solution. **For low level PAHs**

use 1.0 mL of the 1.0ppm LLPAHs spiking solution. Someone must verify that the spike has been added by placing a check mark on each label as it is added.

Enter the ID# of the surrogate/spike used and the initials of the person that verified their addition to the sample in the BNA logbook.

8. **ACID EXTRACTION:** Adjust the pH to between 1.0 and 2.0, using 2 mL of 1:1 H2SO4. Add to each sample, spike and method blank. Stopper and shake to insure that pH throughout the sample is changed. Check the drop of liquid hanging from the lid with short-range pH paper. Compare the color to the chart on the pH paper. If the color is not within range add more H2SO4 solution in small increments, as required to attain the proper pH.

9. Add 40 mL of Methylene Chloride to each empty sample bottle and to the LCS, method blank and MS/MSD funnels. Swirl the 40-mL of methylene chloride that you added to the empty sample bottle and transfer to the corresponding separatory funnel.

10. Seal and shake the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure. Alternatively, Teflon funnels may be used and placed in the shaker apparatus with the stopcocks slightly open. When this apparatus is used, the shake should be for 3 minutes.

    NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once.

11. Allow the sample to sit for 10 minutes, if necessary, after it has been shaken. It will separate into two layers with the solvent layer on the bottom. If it forms an emulsion (thick, cloudy, viscous, mixture that you cannot see through), drain what you believe to be 40 mL into a 250 mL centrifuge bottle. If the layers are clearly separated, drain the solvent layer into a 400-mL glass beaker.

12. Following Steps 9 and 10, extract two more times with 40 mLs of methylene chloride. Combine the three solvent extracts into the same 400-mL beaker.

13. **BASE NEUTRAL EXTRACTION: Adjust the pH to 11 or slightly greater**, using 10N NaOH. Start by adding 5.0 mLs to each sample, spike, and method blank. Stopper and shake to insure that pH throughout the sample is changed. Check the drop of liquid hanging from the lid with short-range pH paper. Compare the color to the chart on the pH paper. If the color is not within range add more 10N NaOH in small increments, as required to attain the proper pH. **BNA extraction is necessary when doing low level PAHs.**

    NOTE: This step is critical to the extraction procedure. Too much NaOH solution could cause you to lose certain Base Neutral compounds. Be careful on this step.

14. **FOR 8270 extraction**: Extract one more time with 40 mL of methylene chloride following Steps 9 and 10. Combine BN and Acid extracts in a same 400ml beaker, unless the BN extract has large amount of emulsion; then it will be necessary to use a separate 400 mL beaker. Concentrate BN and acid extracts for one final extract.
NOTE: It has been demonstrated that two acid and one BN extraction can be used for normal 8270 samples. This procedure cannot be used for DOD or 625 samples.

For 625 extraction: extract 3 more times with 40 mL methylene chloride following steps 9 and 10. Combine BN extracts in separate 400 mL beaker. Concentrate BN and acid extracts separately for one final extract.

15. In the log book marked BNA extractions, enter the Client name, the Lab #, the date extracted, the initial volume, and 1.0 mL for the final volume and anything unusual that may have occurred with this sample. The final volume for low level PAHs is 0.5 mL.

16. Prepare to dry the sample by either of the following methods:
    16A. Get a ring stand with a double burette clamp attached to it. Cover the burette clamp ends with aluminum foil to prevent the possibility of solvent touching the plastic coated ends and dripping into the extract. Place a drying column into the burette clamp and transfer a small amount of glass wool to the top of it. Tamp it to the bottom with a glass rod so that it adequately covers the hole at the bottom. Add approximately 10 cm of Sodium Sulfate to the column. Rinse with 20 to 30 mL of methylene chloride and discard this rinse into the Chlorinated Waste container in the hood. OR

    16B. Set up a ring stand with funnels. Place a small amount of glass wool in the bottom of it, add ~2" sodium sulfate to the column and rinse with 20-30 mL methylene chloride. Discard this rinse into the Chlorinated Waste container in the hood.

17. If the extract was drained into a centrifuge bottle, at this point you will need to take it to the centrifuge. Push the "ON" button to turn the centrifuge on. Be sure that the large holders are available for the 250-mL centrifuge bottles. The sample must always be balanced. If necessary use a dummy bottle making it similar weight using reagent water. Set the rpm at 2500 and the temperature at 0°C. Close the lid and be sure to press it down until you hear it click. Move the lever at the front of the lid to the "LOCK" position. Turn the time to approximately 15 minutes and bring it back to 10 minutes. As the rotor begins to move, you will be able to see the rpm's in the digital readout. Stay with the centrifuge until it has come up to the rpm's set to insure that it does not become unbalanced. This looks like 8888 on the digital readout. Should this occur, refer to the manual. When the cycle is complete, the digital readout will read 0000. Push the "OPEN" button and the lid will pop up. Move the lever at the front of the lid to the "UNLOCK" position. Open lid and remove sample. The sample will usually be in two layers with the extract on the bottom.

18. Remove any water layer from the extract in the beaker or centrifuge bottle, by one of two methods. Remove with a Pasteur pipette by carefully pulling up the water layer, on top, and not the solvent. Discard this layer in the sink. Use the smallest amount possible of Na2SO4 by sprinkling the top layer with Na2SO4 until it hardens, separates, and drops to the bottom.

19. TURBO-VAP CONCENTRATION

Low level PAH sample concentration is primarily done by Turbo-Vap using Round-Bottom TV tubes.

- Rinse a Turbo-Vap tube with methylene chloride and arrange it underneath a rinsed, packed drying column or funnel. Pour the extract through the column so that it will collect in the tube. Rinse the 400-mL beaker, which contained the solvent extract twice with 10 to 15 mL of methylene chloride and add each rinse to the column to complete the quantitative transfer. After all the extract has passed through the column, rinse the column with 10 to 15 mL of methylene chloride. Total volume in the glass evaporator tube should not exceed 200 mLs to avoid splattering on the lid of the Turbo-Vap.
- Record the numbers of the Turbo-Vap tube in the BNA logbook and remove the tube to a metal holder. To help prevent cross contamination, place a piece of aluminum foil over the Turbo-Vap tube and punch a small hole in the top so that the nitrogen can be accessed.

- Turbo-Vap Operation: Adjust the pressure of nitrogen gas tank to >30 psi. Make sure the tank has 200 psi or more on the main valve. The temperature of the bath should be approximately 40°C -50°C.

- Place the glass evaporator tube in the Turbo-Vap. Be sure to push tube down so the tip slides into the sensor well. Close the lid to start concentration. Check that each position with a tube has an orange light showing. If the orange light is not steady, bubbles may be in the sensor and need removal. (See Turbo-Vap manual).

- When the beep sounds indicating the end of concentration, the extract will be at approximately one half mL (half way up tip of tube). Remove the tube from the bath. Use a 9" Pasteur pipette to draw up the sample and transfer it to the 2-mL vial. THIS IS THE MOST CRITICAL PART OF THE ENTIRE OPERATION!!! A single drop represents about 10 percent of the total sample. Before you move the tip of the pipette from the tube to the vial, be sure that a drop will not form on the end and fall off.

- Draw ~0.25 mL of methylene chloride into a 0.50 mL syringe and add this aliquot to the centrifuge tube. Draw the methylene chloride into a pipette and rinse the sides of the tube several times. Transfer this rinse to the 2-mL vial. Add methylene chloride from the syringe and repeat the rinsing process until you have ~ 1 mL in the sample extract vial. Compare this volume to a

2-mL dummy vial containing 1 mL of solvent to insure that you have not exceeded 1 mL. For low level PAHs the final volume is 0.5mL. The methylene chloride rinse volume must be adjusted to achieve this final volume. Compare the volume to a 2mL dummy vial containing 0.5 mL of solvent to insure that you have not exceeded 0.5 mL. The GC/MS operator will adjust the sample to the desired final volume and add internal standard just prior to analyses. Cover the extract with a Teflon-sealed screw cap and transfer the label to the vial.

20. Determine the original sample volume by refilling the sample bottle to the mark made with "white out." Transfer the liquid to a plastic 1000-mL graduated cylinder and record the sample volume in the BNA logbook and the Avery label to the nearest 10-mL.

21. The extract is now ready to be analyzed. Refrigerate at 4°C or carry directly to the instrument operator. Samples must be signed into the Sample Extract refrigerator. On log provided, enter the sample numbers, the analyst initials, and the date and time the samples were placed into the refrigerator.

VI. DOCUMENTATION OF CAPABILITY (DOC)

Each analyst must perform a DOC to demonstrate proficiency with this method. Refer to SOP-413 for guidance.

VII. WASTE MANAGEMENT AND POLLUTION PREVENTION

Please see Waste Disposal SOP-405 for the proper disposal of waste generated from this area.

Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

VIII. METHOD PERFORMANCE

Refer to SOP-201 for method performance.

IX. HEALTH AND SAFETY

Refer to the MSDS sheets for the chemicals used for health and safety information. Also see SOP-336 for proper use of methylene chloride.

REFERENCES

1. *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition
2. 40 CFR, Method 625.

DEFINITIONS

BNA- base/neutral acid
°C - degrees centigrade
COC - chain of custody
DL - detection limit
g - grams
KD - kuderna danish
LCS - laboratory control sample
µg/L - micrograms per liter
µL - microliter
µg/ml - micrograms per milliliter
ml - milliliter
mm - millimeter
MS - matrix spike
MSD - matrix spike duplicate
PAH- polynuclear aromatic hydrocarbon
RL - reporting limit
SOP - standard operating procedure
v/v - volume to volume

Refer to SOP-431 for further definitions

Fraction: Semi-volatiles Matrix: Water EX0__

Supervisor_____

#	Client	Lab No.	Date Extracted	Setup Initials	pH	Initial Volume(ml)	Final Volume(ml)	Surrogate Added	Surr Initials	Spike Added	Spk Initials	KD	10ml Conc.	15ml Cent.	Conc. Initials	Solvent Lot/Vendor Methylene Chloride	Notes/Comments	#
1										NA	NA							1
2										NA	NA							2
3										NA	NA							3
4										NA	NA							4
5										NA	NA							5
6										NA	NA							6
7										NA	NA							7
8										NA	NA							8
9										NA	NA							9
10										NA	NA							10
11										NA	NA							11
12										NA	NA							12
13										NA	NA							13
14										NA	NA							14
15										NA	NA							15
16										NA	NA							16
17										NA	NA							17
18										NA	NA							18
19										NA	NA							19
20										NA	NA							20
								SAS	SAS							SAS		
								SAS	SAS							SAS		
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								SAS	SAS							SAS		

SOXHLET EXTRACTION -

BNA AND PEST/PCB

USING SW846 METHOD 3541

SOP NUMBER: **SOP-329**

REVISION NUMBER: **15**

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: **04/14/08**

DATE OF LAST REVIEW: **04/14/08**

BNA& Pesticide/PCB NON-AQUEOUS MATRIX (Soxhlet Extraction) USING SW846 METHOD 3541

I. SCOPE AND APPLICATION

1. This SOP describes the extraction of BNAs and pesticides/PCBs from soil, sediment, sludges and waste solids by an automated method (3541).

II. SUMMARY

1. Soil and solid samples are mixed with sodium sulfate and extracted with solvent in a Soxtherm extractor for BNAS or Pesticides/PCBs.. The extracts are then concentrated by either a TurboVap concentrator or by Kuderna- Danish.

III. INTERFERENCES

1. Solvents, reagents, glassware, and other sample processing apparatus can add interferences to sample analysis. Method blanks must be extracted under the same conditions as samples to demonstrate freedom from interferences.
2. Phthalate esters commonly found in plastics can interfere with the analysis. Plastics should be avoided.
3. Soap residue can degrade certain analytes such as aldrin and heptachlor. Glassware should be solvent rinsed to avoid this problem.

IV. APPARATUS AND MATERIALS

- Stainless steel spatula
- Soxtherm automated extractor unit-with 6 position condenser assemblies, internal plumbing, electronic components, stand alone controller unit and a copper collection tank for spent solvent
- Soxtherm extraction beakers-54 x 130 mm, capacity approximately 125-175 mL
- Suitable thimble (33 mm diameter by 80 to 94 mm length cellulose or equivalent
- Drying Column (Chromatographic column) - 20mm I.D. x 300mm
- Boiling chips - Teflon
- Vial – 2-mL amber with Teflon-lined screw cap
- Vial – 12-mL clear with Teflon-lined screw cap
- Syringe - 1 mL, 500 µL
- Graduated cylinder - Glass, Class A, 100 mL
- Pasteur pipette - length 9" and 5-3/4"
- Pasteur pipette bulb
- Labels - Avery
- Ring stand - 3 prong
- Burette clamp - double
- Rings

- Aluminum foil - heavy duty
- Nitrogen tank - equipped with pressure regulator
- TurboVap Concentrator with 200 ml concentrator tubes
- Balance - capable of weighing to 0.1 grams.
- Aluminum pie pans for mixing samples
- Glass wool- Contaminant free.

V. REAGENTS

- Sodium Sulfate (Na2SO4) - Granular, anhydrous, trace pure 10-60 mesh (purchased in bulk containers from Fisher # S415-10S or equivalent) placed in a Pyrex tray and heated at 400 C for a minimum of 4 hrs, removed and then cooled in open air in the extraction lab, placed in a 2.5kg glass amber jug and left at room temperature.

- Glass Wool - Silane Treated (purchased from Supelco #2-0410 or equivalent).

- Methylene Chloride **(Please read SOP-336 before handling this solvent in our laboratory.)** (Dichloromethane) - suitable for spectrophotometry and gas chromatography (Omnisolv #DX0831-1 or equivalent)

- Acetone - suitable for spectrophotometry and gas chromatography (Omnisolv AX0116-1 or equivalent)

- Hexane - suitable for spectrophotometry and gas chromatography (Omnisolv HX0298-1 or equivalent)

- Hexane/Acetone (1:1) (v/v) of the above reagent grades.

- Methylene Chloride/Acetone (1:1) (v/v) of the above reagent grades.

- Surrogate/Spike Solutions - Verify the amount of surrogate/spike to add to the sample prior to addition. It can change if a different detection limit is required or the volume of sample being analyzed changes or if the initial concentration of stock is different than that listed below:

  1. **BNA Surrogate (100 ug/ml)** - The base neutral and acid surrogates are mixed together in one solution. This solution is prepared in methanol by making a dilution of stock purchased from a reputable vendor. Use 0.5 mL of this solution per 15g of non-aqueous sample. **(For low level PAHs use 1.0 ml of 1.0 µg/mL BN Surrogate spiking solution.)**
  2. **BNA Spiking Solution (100 ug/ml)** - The base neutral and acid spiking solutions are mixed together in one solution. This solution is prepared in methanol by making a dilution of stock purchased from a reputable vendor with same compounds as for calibration. Use 0.5 mL of this solution per 15g of non-aqueous sample.**(For low level PAHs use 1.0 ml of 1.0 µg/mL PAH spiking solution.)**

3. **TCMX/DCB (2,4,5,6-Tetrachloro-meta-xylene/Decachlorobiphenyl)Warm and sonicate** - Surrogate solution is prepared in acetone by making a cut on stock purchased from a reputable vendor. 0.5 mL at 0.5 µg/mL of this solution is added per 15g of non-aqueous sample.
4. **PCB Spiking Solution-** Arochlor 1016/1260 or the PCB of choice (1242, 1248, 1254, or 1260 are the most common) is prepared in acetone at a concentration of 5.0 ug/ml. PCB stock is usually purchased from RESTEK or equivalent. The PCB to use may be determined by viewing historical data or asking the GC operator. Use 0.5 mL per 15.0 grams of non-aqueous sample.

5. **Pesticide Spiking Solution** - A spiking solution is prepared at 1.0 ug/ml. Use 0.5 mL per 15 grams of non-aqueous sample.

VI. SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

1. Samples are collected in an appropriate size wide-mouth glass jar (4oz. or 8 oz.) with a teflon-lined cap.
2. Samples are preserved by cooling to 4° C.
3. Holding time is 14 days from collection date to extraction.

VII. PROCEDURE

Extraction Procedure

1. All soils have a 14 day holding time counted from the day they are sampled.Determine the samples necessary to extract using the following information (DO NOT extract samples for which you have no information.):
   - Each day a backlog report will be provided indicating sample numbers with the respective analysis required. Line through all the extractions that have been completed and plan to do the remaining analysis within the required holding time.
   - Samples requiring RUSH turn around time may be logged in throughout the day which will require your immediate attention. Log-in personnel will generally communicate this need.
   - Check with log-in throughout the day and examine the COC (chain of custody) forms that arrive with each set of samples. If an analysis is ongoing, extra QC may be avoided by picking up those extractions on the same day.

2. Wearing lab coat, gloves and safety glasses, get samples from cooler. Samples must be signed out of the walk-in refrigerator. Enter the sample numbers, your initials and the date and time removed on the log provided. Inspect as to whether they are in glass and have a Teflon lid. Find out if any special dilutions need to be made for this client. If the sample has a particularly bad matrix or a strange matrix, see your supervisor to find out if a soxhlet extraction is truly necessary.

3. Get twice the number of aluminum pie pans to prepare the number of samples you have plus any additional spikes or LCSs and a method blank. A method blank and LCS must be processed with each set of samples. A matrix spike, a duplicate or a matrix spike duplicate and a LCS must be processed for each analytical batch (up to a maximum of 20 samples). Make an Avery label for each extract containing the following information: Lab #, Client name, Type of Analysis, Initial Weight - Final Volume, and the Lab prep batch code. The lab prep batch code for BNAs is defined as MMDDYYBs# where #: 1 = 1st method blank of the day; 2 = 2nd method blank of the day; etc. The lab prep batch code for Pest/PCBs is defined as MMDDYYPs# using the same logic. The Method Blank and LCS labels must include all lab #s in this set of samples.

4. Decant and discard any water layer on a sediment sample by carefully pouring this off into a trashcan.

5. Dump the entire sample into an aluminum pie pan and mix sample thoroughly with a spatula until mixture is homogenous. Discard any foreign objects such as sticks, leaves, and rocks.

It is extremely important that waste (when appropriate), soil and sediment samples be mixed thoroughly to ensure that the sample is as representative as possible of the sample media. The most common method of mixing is referred to as quartering. The quartering procedure should be performed as follows:

- *The material in the sample pan(inorganic-plastic/organic-aluminum) should be divided into quarters and each quarter should be mixed individually.*
- *Two quarters should then be mixed to form halves.*
- *The two halves should be mixed to form a homogenous matrix.*

This procedure should be repeated several times until the sample is adequately mixed.

NOTE: Samples that are clay type materials should be handled in a different manner. Due to these type sample matrices having an affinity to stick to most anything that touches it, another approach must be followed. Obtain a representative sub-sample aliquot from the center or middle section of the sample container

6. Place an aluminum pie pan on the balance and zero it. Calibrate balance with ASTM class-1 Troemner weights or equivalent, bracketing desired weight (50g, 20g, 10g, 5g, 1g). Record calibration in the Extraction calibration/temperature logbook. Using a spatula, transfer the **appropriate weight, {10-20 grams depending upon client or project specific Detection Limits (DL) and/or Reporting Limits (RL)}**, of a representative sample to the nearest 0.1 gram. Normally 10 or 15 gram sample weights are used. Record this amount on your label. Put your label on the side of the 400-mL beaker. For spiking purposes, weigh 3 aliquots of the appropriate sample. Pick a sample with a good matrix, one that mixes well, non-oily, etc.

7. Add ~ 20 grams of sodium sulfate to the aluminum pie pan. Using a spatula and/or a glass rod, mix the sample thoroughly with the sodium sulfate until it becomes a sandy texture. If necessary, add additional sodium sulfate. When removing the spatula or glass rod from the mixed sample, leave behind all the sample possible. Cover the aluminum pie pan with foil and continue to weigh up the remaining samples. For the method blank and LCS, simply weigh up 15 grams of sodium sulfate. The matrix used for the method blank and LCS must be free of the analytes of interest and processed through the same analytical steps as the samples.

8. Transfer the sample and its label to a soxtherm beaker, which has been prepared using a glass rod to place glass wool in and over the hole at the bottom side.

9. Make up 1:1 Methylene Chloride/Acetone (**for BNAs**) or 1:1 Hexane/Acetone (**for Pest/PCBs**) by mixing 2000ml of methylene chloride or hexane with 2000 ml of acetone in a 4000ml amber jug. Add 120 mL of this mixture to the soxtherm beaker for each sample, method blank, and spike - add boiling chips.

10. Verify the amount of surrogate/spike to add to the sample prior to addition. It can change if a different detection limit is required or the volume of sample being analyzed changes. Set out the surrogate/spike at least ten minutes before use to allow it to warm to room temperature. Someone must verify that the surrogate/spike has been added by placing a check mark on the label as it is added.

    NOTE: Surrogate and spike should be added just prior to setting on the Soxtherm.

    Using the 1-mL glass syringe designated for BNA surrogate, add 0.5 mL of BNA surrogate to each sample, spike, and blank. **(For low level PAHs use 1.0 ml of the 1.0 µg/mL BN Surrogate spiking solution.)** or using the 1.0-mL glass syringe marked TCMX/DCB surrogate, add 0.5 mL of TCMX/DCB surrogate to each sample, blank and spike.

    For the BNA sample in each analytical batch selected for spiking, use the 1.0-mL glass syringe marked Base Neutral Acid Spiking to add 0.5 mL of the Base Neutral Acid Spiking solution. . **(For low level PAHs use 1.0 ml of the 1.0µg/mL PAH spiking solution.)**
    For Pest/PCB samples, determine if the sample will require a Pesticide Spike and/or a PCB Spike. Proceed as follows:
    Pesticide and PCB - set up two LCS's – one for Pesticide getting a MIX A&B spike and one for PCB which should be spiked with PCB 1660. In addition to the LCSs, a matrix spike/matrix spike duplicate is necessary for the pesticide. Prepare a PCB matrix spike/ matrix spike duplicate if requested by the client.
    Pesticide only – To the sample in each analytical batch selected for spiking, add 0.5 mL of Pesticide Spike (Mix A&B) with a glass syringe dedicated for Pesticide Spike.
    PCB only - To the sample in each analytical batch selected for spiking, add 0.5 mL of PCB 1016/1260 (unless otherwise specified, 1248 for BB&L) using a 1.0 mL glass syringe dedicated to that PCB. Add 20 grams of Na_2SO_4.

11. **Automated Soxhlet:** The *Soxtherm* will extract any number of samples up to six per run. Generally, we set up to complete four sets of six a day or/as sample load permits with required QC. Each extraction cycle takes 1-2 hours. Reference *O.I. Analytical Operator's Manual* for programming and making adjustments to extraction cycle settings.

- The extraction thimbles are placed into the respective extraction thimble holders(the open end of the thimble is nearly flush with the upper edge of the metal ring. Transfer the sample into the extraction thimble. The appropriate spiking solution should be added at this point (surrogates, MS/MSD or LCS etc…). (Placing a small piece of glass wool sufficient to cover the diameter of the thimble will help hold the sample mixture in the thimble.)

- Place 1-2 boiling chips in each extraction beaker and place each extraction thimble into the appropriate labeled beaker then add 120 mLs of the appropriate extraction solvent. (1:1 Acetone/Hexane for Pest/PCBs **or** 1:1 Acetone/Methylene Chloride for BNAs.)

- For loading samples on the *Soxtherm,* the condensers should be in their raised position. If Viton gaskets are to be used, install them in the extraction beakers so that a good seal will form between the extraction beaker and the Teflon extraction cylinder. Install the extraction beakers by depressing the holding clamp and carefully sliding the beaker onto or off the bottom of the Teflon fitting that is situated below the glass condenser. After the extraction beakers containing the samples have been loaded on the *Soxtherm,* push all beakers against the rear limit stop of the hot plate.

- The *Soxtherm* is now ready to run with one of the programs listed below (**remember to check the sight glass on the front of the Extraction Unit to see if the solvent collection tank is near full and should be drained**).

<u>Pest/PCB Extraction Program</u>

Temperature	= 165°C (Maximum temperature 200°C)
Boiling Time	= 30 minutes
Solution Reduction A	= 5x15 ml
Extraction Time	= 30 minutes
Solution Reduction B	= 0 minutes
Solution Cooling	= 0 minutes
Solution Reduction Interval	= 2.5 minutes
Solution Reduction Pulse	= 2 seconds

<u>BNA Extraction Program</u>

Temperature	= 160°C (Maximum temperature 200°C)
Boiling Time	= 30 minutes
Solution Reduction A	= 5x15ml
Extraction Temperature	= 30 minutes
Solution Reduction B	= 0 minutes

Solution Cooling	= 0 minutes
Solution Reduction Interval	= 2.5 minutes
Solution Reduction Pulse	= 2 seconds

- At the end of Solution Cooling time the condensers and extraction beaker assemblies are automatically raised off the heating block and the process completion message appears on the display. Remove the beakers to a hood and continue with the process as listed below.

13. Enter the following information in the BNA, Pesticide and/or PCB extractions logbook: Client name, Lab #, date extracted, initial weight, final volume, soxtherm position, and anything unusual that may have occurred with this sample. Enter the ID# of the surrogate and spike used and the initials of the person that verified their addition to the sample in the appropriate logbook. Also record the vendor and lot number of the methylene chloride or hexane and acetone used.

14. Dry the sample by either of the following methods:

14A. Get a ring stand with a double burette clamp attached to it. Cover the burette clamp ends with aluminum foil to prevent the possibility of solvent touching the plastic coated ends and dripping into the extract. Place a drying column into the burette clamp and transfer a small amount of glass wool to the top of it. Tamp it to the bottom with a glass rod so that it adequately covers the hole at the bottom. Add approximately 10 cm of Sodium Sulfate to the column. Rinse with 20 to 30 mL of methylene chloride or hexane and discard this rinse into the appropriate waste container (make certain that methylene chloride waste goes in the chlorinated solvent waste container in the hood).

14B. Set up a ring stand with funnels. Place a small amount of glass wool in the bottom of it. Add ~2" sodium sulfate to the column and rinse with 20-30 mL methylene chloride or hexane for Pest/PCBs. Discard this rinse.

15. TURBO-VAP CONCENTRATION

A. Turn on the TurboVap and set the temperature at 40°C -50°C. This temperature is necessary to evaporate the acetone. Adjust pressure of nitrogen gas tank to >30 psi. Make sure the tank has 200 psi or more on the main valve.

B. Rinse a Turbo-Vap tube and arrange it underneath a rinsed, packed drying column/funnel. Pour the extract through the column/funnel so that it will collect in the tube. Total volume in the glass evaporator tube should not exceed 200 mLs to avoid splattering on the lid of the Turbo-Vap. Therefore the process cannot be completed in one step. Pour enough of the extract from the 400 mL beaker to reach the 200 mL level mark on the Turbo-Vap tube. To help prevent cross contamination, cover the turbovap tube with aluminum foil and punch a small hole in the top of it.

A portion of the extract will remain in the beaker. This should be set aside with the funnel used to dry the first portion of the sample placed in the mouth of the beaker.

C. Record the Turbo-Vap tube number, the vendor and lot number of hexane used in the appropriate extraction logbook.

D. Place the glass evaporator tube in the Turbo-Vap. Be sure to push tube down so the tip slides into the sensor well. Close the lid to start concentration. Check that each position with a tube has an orange light showing. If the orange light is not steady, bubbles may be in the sensor and need removal. (See Turbo-Vap manual).

E. When the extract has been concentrated to ~1.0 mL, remove it from the Turbo-Vap and find the remaining extract. Reuse the original funnel and pour the remaining extract through it so that it drains into the turbovap tube. Rinse the 400 mL beaker twice with 10 -20 mLs of methylene chloride or hexane for Pest/PCBs transferring the rinse to the funnel each time. Finally rinse the funnel with ~ 10 mLs of solvent. Place a piece of aluminum foil over the tube and with a sharpie mark an "X" on the aluminum foil. Remove the tube to a metal holder. Concentrate as before.

F. When the beep sounds indicating the end of concentration, the extract will be at approximately one half mL, remove the tube from the bath. The extracts are ready to be transferred into their appropriate vials.

- **For Pest/PCB Completion:** Hold the tube and the sample vial in one hand at about a 45° angle. Use a 9" pasteur pipette to draw up the sample and transfer it to the 10 mL vial. Be careful not to spill any sample during the transfer because one drop represents 5% of the sample and is a critical loss.
- Fill a 10 mL graduated cylinder with 9.5 mL of hexane. Add 1/2 of the hexane to the tube. Draw into the pipette and rinse down the conical portion of the tube several times. Transfer this rinse to the 10 mL vial. Add the remaining hexane and repeat this rinsing process. Cover the extract with a Teflon-sealed screw cap.

- **BNA Completion:** When the volume has been reduced to 1-0.5(~0.4)mL, remove the tube from the Turbo-Vap and place in a metal holder.
- Use a 9" Pasteur pipette to transfer the extract to a 2 mL amber vial. THIS IS THE MOST CRITICAL PART OF THE ENTIRE OPERATION!!! A single drop represents about 10 percent of the total sample. Before you move the tip of the pipette from the tube to the vial, be sure that a drop will not form on the end and fall off.
- Draw ~0.20 mL of methylene chloride into a 0.50 mL syringe and add ~ half of this aliquot to the tube. Draw the methylene chloride into a pipette and rinse the sides of the tube several times. Transfer this rinse to the 2 mL vial. Add methylene chloride from the syringe and repeat the rinsing process until you have ~ 1 mL in the sample extract vial.

- Compare this volume to a 2 mL dummy vial containing 1 mL of solvent to insure that you have not exceeded 1 mL. For low level PAHs the final volume is 0.5mL. The methylene chloride rinse volume must be adjusted to achieve this final volume.

Compare the volume to a 2mL dummy vial containing 0.5 mL of solvent to insure that you have not exceeded 0.5 mL. The GC/MS operator will adjust the sample to the desired final volume and add internal standard just prior to analyses. Cover the extract with a Teflon-sealed screw cap and transfer the label to the vial.

NOTE: If the final extract is yellow or dark in color or the matrix is oily and viscous, further cleanup may be desired. Refer to SOPs 307 to 309 and 330, 331, 333 for further cleanup information. Discuss cleanup possibilities with the analyst and/or your supervisor.

The extract obtained above may now be analyzed. Refrigerate at 4°C or carry directly to the analyst. Samples must be signed into the Sample Extract refrigerator. On log provided, enter the sample numbers, your initials, and the date and time the samples were placed into the refrigerator.

VIII. DOCUMENTATION OF CAPABILITY (DOC)

Each analyst must perform a DOC to demonstrate proficiency with this method. Refer to SOP-413 for guidance.

IX.. WASTE MANAGEMENT AND POLLUTION PREVENTION

Please see Waste Disposal SOP-405 for the proper disposal of waste generated from this area.

Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

X. METHOD PERFORMANCE

Refer to SOP-201 and SOP-211 for method performance.

XI. REFERENCES

1. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846; Third Edition (Update III)*; Method 3541.

DEFINITIONS

BNA - Base/ Neutral/Acid
°C - degrees centigrade
COC - chain of custody
DL - detection limit
g - grams
KD - kuderna danish
LCS - laboratory control sample
µg/L - micrograms per liter
µL - microliter
µg/ml - micrograms per milliliter
ml - milliliter
mm - millimeter
MS - matrix spike
MSD - matrix spike duplicate
PAH - polynuclear aromatic hydrocarbons
PCBs - polychlorinated biphenyls
Pest - pesticides
RL - reporting limit
SOP - standard operating procedure
TCMX - tetrachloro-m-xylene
v/v - volume to volume

Refer to SOP-431 for further definitions

LABORATORY SAMPLE RECEIVING, LOG IN AND STORAGE STANDARD OPERATING PROCEDURES

SOP NUMBER: **SOP-404**

REVISION NUMBER: **11**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: **05/02/08**

DATE OF LAST REVIEW : **05/02/08**

LABORATORY SAMPLE RECEIVING, LOG IN AND STORAGE

This SOP lists in as much detail as possible our daily procedures for sample receiving, log in and storage of laboratory samples. Keep in mind that there may be project specific requirements that are more strict or different than our routine procedures. In these instances, the project specific requirements must be met and followed. Although a few project specific requirements are detailed in this SOP, i.e. USACE certification issues, not every situation can be addressed. If there is ever any uncertainty on what procedures must be followed, please see the Testing Coordinator immediately. If ever in doubt, always go with the more stringent requirements. This document will constantly be reviewed and revised as necessary.

SAMPLE ACCEPTANCE CRITERIA

A sample should be rejected for compliance purposes if it does not meet the following criteria. Analyses may only proceed after notification and approval to proceed from the client.

1. Sample must be properly preserved and in the proper container for the requested analysis.
2. Sample integrity must be maintained. The container shall be intact without cracks, leaks, or broken seals.
3. Adequate sample volume must be received for the requested analysis, including volume for any necessary QA/QC (MS/MSD).
4. The sample ID on the bottle label must match the sample ID listed on the chain of custody.
5. The sample container label and the chain of custody must be completed with indelible ink. The sample label must be intact and list all necessary information; to include: sample date, sample time, sampler, and sample ID/location. The chain of custody shall also indicate sample date and time, requested analyses, and all necessary client information.
6. Sample temperature must be less than 6°C.
7. Sample must be within holding time for the requested analysis.

These issues are discussed in more detail below under the "Sample Receiving" section of this document.

I. Sample Receiving

A. Samples are received at the Empirical Laboratories on French Landing Drive in Nashville, TN.

1. The majority of samples are shipped in coolers by couriers such as Federal Express and UPS. All couriers are generally received in the Empirical Laboratories Sample Receiving (SR) area on the fifth floor. The laboratory is located close to the Federal Express (FedEx) distribution station, therefore we often pick up our coolers at the FedEx location and transport them back directly to the laboratory. Some coolers and/or samples are delivered directly to the SR area by the sampler and/or client.

2. Some coolers and/or samples may be received directly by Empirical Laboratories Sample Receiving personnel. If samples are hand delivered by the client make sure that necessary paperwork is included and that you sign and date the chain of custody. If the *Empirical Laboratories* ***Chain of Custody [Attachment II***] is used the white and yellow copy of the chain of custody is retained and the pink copy must be given to the client.

B. When going through the required steps for Sample Receiving and Sample Log In, keep in mind that a ***Corrective Action Report (CAR) for Sample Receiving [Attachment III]*** must be completed to document any problems, discrepancies, project changes, etc. encountered during the process. This includes but is not limited to incorrect sample containers, improper preservatives [chemical and temperature], chain of custody discrepancies, sample descriptions, etc. A CAR may be completed just to keep a record of a situation, which is not actually "out of compliance."

1. Make sure that all information on the CAR is stated clearly and very detailed. Many times it is necessary to refer to these documents a year or more after they were completed. Document all correspondence including name, date, company and response.

2. The CAR forms must be numbered starting with No. 001 at the beginning of the year (e.g. 01-001). No two forms should have the same number. All CARs must be forwarded to the Project Manager and/or receiving manager for approval and distribution. THIS MUST BE DONE ASAP OF WHEN THE PROBLEM/SITUATION IS DISCOVERED.

C. Visually inspect all coolers for tampering, custody seals present and intact (if applicable) leakage, etc. If a cooler has been damaged, unpack the samples and discard the cooler as to not reuse it. If you suspect a cooler may be damaged or is extremely dirty this cooler must not be reused. If coolers were sent by Federal Express, examine the Federal Express airbills for the number of packages in the shipment and make sure that all the packages (coolers, boxes etc.) in a group have been received. If there are any problems the Project Manager must be contacted immediately. If anything looks unusual, take the time to check it out and document the situation and findings.

D. Open each cooler in order to quickly inspect the contents and to locate the chain of custody. Sample Receiving personnel should wear the following personal protection equipment: gloves, safety glasses and a laboratory coat. All coolers received from projects with the **US Army Corps of Engineering (USACE) and AFCEE** projects should be opened under the hood in the sample storage room. Sign, and list the date and time received on the chain of custody. The time received <u>must</u> reflect the actual time the samples were received even though they may be logged into the system at a later time. Samples received on Saturday may be processed on the following Monday morning, or samples received late in the day during the week may be processed the next morning. All cooler(s) <u>must</u> be opened, examined for leakage, breakage etc., the temperature measured and the chain of custody signed and dated to reflect the actual date and time which they were received. The samples must be put in cold storage as soon as possible.

1. Attach any shipping receipts, work orders, etc. to the chain of custody.

2. If a chain of custody or other paperwork is not sent, the client must be contacted and the samples temporarily placed on hold in cold storage. In some instances the log-in person may complete a chain of custody. The required information may be found on the sample containers or it may be necessary to call the client to get the missing information (i.e. sample ID, collection date and time, etc.). Note on the chain of custody that it was completed by laboratory personnel and record the name of the person with whom you spoke. All attempts to encourage our customers to complete a chain of custody or submit written information for samples must be made.

3. Project specific paperwork may be required. For all USACE and USCLP projects, a ***Cooler Receipt Form [Attachment IV]*** must be completed for each cooler received. Sample receiving personnel must begin completing this form as soon as a cooler is received and complete this form as samples go through the log in process.

E. The temperature of each cooler or set of samples must be measured as quickly as possible using a thermometer with 0.1°C increments. This thermometer must be calibrated against a NIST certified thermometer once a year and this information recorded in a bound notebook. The Certificate of Calibration for the NIST thermometer is kept on file at the QAO's desk. The thermometer must be tagged with the unique identification number of SR#1 and serial #; (Sample Receiving #1), the date calibrated and the correction factor. This information must also be recorded in a bound notebook. Only this thermometer can be used for recording the temperature of sample coolers upon receipt.

1. To measure the temperature, open the temperature control blank, point the IR thermometer at the liquid surface, wait 30 seconds for temperature to stabilize. Read the temperature to the nearest 0.1 °C. The corrected value temperature must also be recorded on the chain of custody. (This value will also be recorded into the LIMS at a later point.). All regulatory compliance samples received from North Carolina that do not meet the temperature requirement will be segregated and the North Carolina State Laboratory will be notified of the non-compliance (919-733-3908). The samples will not be logged in or analyzed until written notification is received from the State of North Carolina to proceed with analyses.

2. If a cooler is received with no temperature control blank bottle, pour up a small aliquot of sample from one of the sample containers (unpreserved if available) in the cooler and measure this as the temperature control sample. Discard this aliquot after the reading. If only VOA vials are received check with the Project Manager or Section Manager before opening any of the vials. If any sample is taken from the VOA vial for temperature measurement, the entire vial must be discarded. If non-aqueous samples are received without a temperature control blank then the temperature of the cooler itself can be monitored by placing the thermometer directly in the cooler. This should be noted.

3. If the temperature exceeds 6°C for any sample, the Project Manager or Sample Receiving personnel must contact the client immediately. There may be tighter temperature control limits for specific project requirements. The customer must make the decision to either continue with the analyses or resample. Make sure the client is aware that if the samples are analyzed, the following qualifier is normally included on the final report: "The shipping cooler temperature exceeded 6°C upon receipt to Empirical Laboratories. This may have an impact on the analytical results. The concentration may be considered as estimated." Not all samples for the project will be flagged, just those samples received above 6°C.

   Many times we are not able to get in touch with the client quickly and the best judgment on how to handle the samples must be made after discussion with the Testing Coordinator and/or Laboratory Director or Technical Director. The samples may still need to go through the log in process although it may be eventually determined that the samples will not be analyzed or the samples may temporarily be placed on hold and not logged in. Above all do not allow the samples to set out at room temperature for an extended period of time while waiting for a decision. **A CAR outlining the problem and all correspondence must be completed.**

   The only exceptions to the 6°C rule are:

   a. Water samples for all Metals, (except Chrome 6+ and mercury) that have been preserved with HNO_3 to a pH of ≤ 2. *Keep in mind that non-aqueous sample for Metals must be cooled.*

   b. Samples for Fluoride, Chloride and Bromide.

   c. Waste/Product samples for all parameters.

   d. Samples generated in the Aquatic Toxicology laboratories and brought directly to Sample Receiving after they are collected. Sample receiving personnel should place these in cold storage as soon as possible.

   e. Samples collected locally by Empirical Laboratories personnel or local customers that hand deliver their samples. In some instances these samples may not have had time to cool down, however, these samples should have been placed on ice in an attempt to cool them to the proper temperature. It should be noted if samples are "Received On Ice" (ROI).

F. If several coolers are received at once, they must be inspected to determine the order in which the samples should be unpacked and logged in. The following priorities should be given:

   1. Any analyses, which have a 24-72 hour holding, time. A ***Short Holding Time Parameter List [Attachment V]*** is posted in the log-in room. It is the log-in person's responsibility to notify the analyst of such samples. In addition to notifying the analyst of samples with

short holding times, log-in personnel must log this information into a separate record book daily. It is the analysts' responsibility to review this information and initial each page at the end of each day.

2. Any sample which has almost exceeded its' holding time. (Especially watch for this with waters organic extractions, Solids and Sulfides, all of which have only 7 days). A list of parameters and holding times is posted in the log-in room.

   a. If a sample is received already out of holding time, the project manager must be contacted. The sample can be analyzed at the client's request, but it will be qualified on the final report as being analyzed out of holding time. The project manager must inform you of the client's need.

   b. If a sample is received with limited holding time remaining for any parameter it may be necessary to contact the project manager so that he/she can contact the client. If the sample has to be analyzed on a rush basis to meet the holding time a rush charge may apply. Also it may not be possible to analyze the sample within the holding time due to sample load, etc. A CAR must be completed.

3. Samples requiring rush turnaround.

   a. If sample(s) requires 24-hour turnaround they will take first priority. Other rush requests also have high priority.

   b. The Project Manager and/or Section Manager must be contacted for approval concerning any unscheduled rush requests.

G. Unpack all samples from the cooler. If there are any known or suspected hazards this must be done under a hood. All coolers from USACE projects should be unpacked under a hood. It may be necessary to rinse off the outside of the containers in the sink and/or wipe them off with a paper towel.

1. Visually inspect them for tampering and custody seals (if applicable). Sort and inventory the samples against the chain of custody by arranging them in the same order as they are listed on the chain of custody. Normally samples are assigned log numbers in the same order as they are listed on the chain of custody but for certain projects or situations it is acceptable to arrange them in a manner which will make them easiest to log in.

2. Check for leakage as this could compromise the sample integrity. If any spillage occurred in the cooler make sure this is noted. Also list all the other samples in the cooler as cross contamination could occur. A CAR must be completed and the Project Manager and/or the customer may need to be notified in these situations. It may be necessary to resample.

H. Check the chain of custody information against the information recorded on the containers. If these do not agree, contact appropriate person (s) - Project Manager, sampler, client, etc. All problems must be documented with a CAR.

1. If major changes are made on the chain of custody received from an engineering job, then the PE should submit written confirmation of these changes or make the corrections and initial them directly on the chain of custody.

2. Any error found on the chain of custody must be marked through with one line, initialed and dated and the correction written in.

I. Note any unusual requests, methodology, hazards (known or suspected) to the Project Manager and/or Laboratory Section Manager or analysts before the samples are actually logged in. Keep notes of any problems (improper containers, preservatives, temperature, or descriptions, etc.) A CAR must be completed but can be done so later in the day (see section IIIC), however, the analyst or manager may need to be notified immediately. If ever in doubt, fill one out!

II. Sample Log In

A. After samples have been unpacked, sorted and reviewed, they are then ready to be assigned log numbers and continue through the log in process. Make sure that the parameters for the samples are clearly marked on the chain of custody. Also refer to the "Incoming Project" file or routine client notebook in the log-in room to see if there is a work order or a memo to help you log in these samples. If we prepared the sample kits there should be a sample kit work order form. Contact the Project Manager if there are any questions, problems, etc.

B. Assign a work-order and sample number to each individual sample and record it on each sample container and the chain of custody.

1. All containers with the same description must have the same sample number even if they have different preservatives and require different tests. However, each different fraction (bottle type and/or preservative) should be designated with a letter (A, B, C, etc.)

2. Grab and composite samples from the same sample location must be considered as separate samples. It may be necessary to use "grab" or "composite" as part of the sample description to distinguish between the samples. Only assign different log numbers to them if the parameters are clearly marked as grab and as composite. Do not assume that VOC must be analyzed from grab samples so therefore the client must have taken a grab sample.

3. Sample numbers must begin with 001 at the beginning of each year (e.g. 0101001).

C. Check the following items and record this information on the chain of custody to further ensure sample integrity. A CAR must be completed if any of the following requirements are not met and it may be necessary to contact the client. We can perform the analyses in most cases and will do so with the client's approval, however the results may be qualified in some manner on the final report.

Preserving sample integrity throughout the log in procedure must be one of our section's top priorities. This includes not only ensuring that the proper chemical preservatives have been added but also that the samples are received and maintained at the proper temperature. ***When samples are unpacked they must be placed in cold storage as soon as possible even if they have not been through the entire log in procedure***. All samples for NPDES compliance monitoring from North Carolina will be stored at a temperature range of 1.0 to 4.4°C. All other NPDES samples will be stored at 4.0 ± 2.0°C. On the days we receive a large volume of samples, or are short handed, etc., we may not be able to completely log in all samples until late in the day or even the next day. Samples should not set out at room temperature if there is a delay. The samples must temporarily be placed in cold storage until you are able to complete the log in procedure. This should also be done when we take lunch breaks.

[Make sure the VOC containers are not temporarily stored in a non designated VOC only storage area.]

1. Determine if the samples were received at the proper temperature. (See section IC)

2. The sample descriptions on the bottle should match those on the chain of custody. (See section 1H)

3. Check to determine if the proper chemical preservatives were added to adjust the sample to the correct pH. All regulatory compliance samples received from North Carolina that do not meet the preservation requirement will be segregated and the North Carolina State Laboratory will be notified of the non-compliance (919-733-3908). The samples will not be logged in or analyzed until written notification is received from the State of North Carolina to proceed with analyses. A list of parameters and the required chemical preservatives is posted in the log-in room. If Empirical Laboratories prepared and shipped out the sample containers they will have been pre-preserved unless instructed otherwise by the client. Complete traceability of the preservatives used to pre-preserve the sample containers and to preserve samples in the log-in area is required. A bound notebook must be used to trace this information and must include the following: Lot #, Type of preservative, Date Prepped, Amount and Analyst Name. This information must also be labeled on each container, re-pipetter, etc. that the preservative is stored in. Each lot of HNO3 used for Metals preservation must be tested prior to using them for preservation. These analyses are kept on file.

   a. The pH of each container (except VOA vials) which requires pH preservation must be checked. Do not open and check the pH of VOA vials in sample receiving/log-in.

This will be done by the VOC analysts at the time of analysis. In some instances it may be necessary to open the sample under a hood.

b. The pH of preserved samples are checked and confirmed using pH narrow range indicator paper. When the client request pH analysis on samples and they must be reported and measured for pH using the narrow range paper, rather then a pH meter, the accuracy of each batch of indicator paper must be calibrated to the nearest tenth versus certified pH buffer and recorded into a bound logbook in accordance with SW846 method 9041A pH Paper method.

c. When taking the pH reading, DO NOT PUT THE pH PAPER DIRECTLY INTO THE SAMPLE CONTAINER. Pour up a small aliquot and dispose of this volume after the pH is taken. For some samples (wastes) the indicator paper may not be accurate due to interferences. The observation of the appropriate color change is a strong indication that no interferences have occurred. If it appears as if there is interference, the pH must be measured using the pH meter. [See SOP ATSD-187 pH , Electrometric.]

4. The following guidelines must be followed to check pH preservation:

a. Water samples for Cyanide analyses must be preserved to a pH of >12 with NaOH upon collection. If the pH of these samples is between 11.0-12.0 upon receipt, and the samples are at the proper temperature and not over 48 hours old it will not be necessary to complete a CAR, however the sample should be adjusted to $\geq$12.0 unless project/client specific requirements are to contact the client first.

b. Water samples for Metals analyses must be preserved to a pH of $\leq$2.0 with HNO_3 upon collection. If the pH of these samples is between 2.0-.3.0 upon receipt, and the samples are not over 48 hours old it will not be necessary to complete a CAR, however the sample should be adjusted to $\leq$2.0. unless project/client specific requirements are to contact the client first.

c. Samples requiring analyses which are preserved with H_2SO_4 (i.e., Nitrogen compounds, Total Phenolics, Oil and Grease, Total Phosphorus, etc.) can be accepted up to a pH of 2.5 without a CAR, however the sample should be adjusted $\leq$2.0 unless project/client specific requirements are to contact the client first. Samples for sulfide analysis must have a pH >9.

d. If a sample is not properly preserved, log-in personnel must either do the following:

- To meet project specific requirements, including all USACE projects, the client must be notified before preserving or adding additional preservative to the sample unless otherwise instructed. If the client instructs us to add chemical preservatives to a sample, complete traceability of the preservatives used is required (See section IIC, #3). A CAR must be completed.

- For other projects it may be acceptable to preserve the sample accordingly before the sample is placed in storage. Complete traceability of the preservatives used is required (See section IIC, #3). A CAR outlining the project and the steps taken must be completed.

e. In some instances it may not be possible to adjust the sample to the proper pH due to matrix problems which cause excessive foaming or require an unusually large amount of acid. Do not continue to add acid if a few mL's of acid does not lower the pH. Notify the Project Manager, Metals Manager and/or analyst. They will make the decision if the sample will be diluted, not analyzed, etc. A CAR must be completed in these situations. Make sure you note on the container and in the LIMS notes that the sample is not at the proper pH as well as any useful information (i.e., foaming, strong odor, etc.).

f. A CAR may not be required for samples generated in the Aquatic Toxicology Laboratories and brought directly to Sample Receiving after they are collected but before they are preserved. Log-in personnel must preserve the samples accordingly before they are placed in storage. Complete traceability of the preservatives used is required (See section IIC, #3). A CAR outlining the project and the steps taken must be completed.

5. Check to make sure samples are in proper containers and that there is adequate volume for all the parameters requested and no leakage.

6. If VOA vials are present, each vial must be inverted and checked for head space. "Pea-sized" bubbles (i.e. bubbles not exceeding 1/4 inch or 6 mm in diameter) are acceptable and should be noted, however a CAR is not required. This guidance is from SW846 Proposed Update II. Large bubbles or head space is not acceptable and a CAR must be completed. If this occurs, the client must be contacted. The samples can be analyzed with their approval, however the report will be qualified and the data may be questionable. All VOA vials will be preserved with $Na_2S_2O_3$ (0.2g) when chlorine is known to be, or suspected to be present.

7. All pesticide samples to be analyzed by method 608 will be checked by the sample receiving personnel for the correct pH range of 5.0 to 9.0. The pH of the sample(s) will be communicated via E-mail to the Section Manager and appropriate analyst.

8. All chlorinated effluent samples received for Cyanide must be checked for residual chlorine. The one liter sample container should initially contain 1 to 2g/L of Ascorbic Acid. <u>Potassium Iodide starch indicator paper will be used for detecting the presence of residual chlorine. DO NOT PUT THE TEST PAPER DIRECTLY INTO THE SAMPLE CONTAINER. Pour up a small aliquot, neutralize, test and dispose of this volume after the sample is checked.</u> If the test paper turns blue, the sample must be treated for residual chlorine. Add Ascorbic Acid, approximately 0.6g at a time and recheck the sample until there is no residual chlorine present. If the sample required this treatment this information

must be included in the LIMS notes. This must be done by log-in personnel before leaving the receiving area. It may be necessary to notify the Inorganic Manager and/or analyst.

9. Be aware of holding time requirements. (See section 1D)

D. Once sample containers have been numbered, they must be checked by another laboratory individual to ensure that the log number on the container matches the log number and sample ID on the Chain of Custody. A ***Sample Receiving Custody and Disposal Form [Attachment VII]*** must be completed each day. Samples should not leave the log-in area until this has been completed. *[see IIC; it may be necessary to temporarily store samples in cold storage until the samples can be second checked, the amount of time that the samples are at room temperature must be minimized as much as possible.]* The original is to remain in Sample Receiving until the samples are disposed of. Once the document is complete, the original will be kept on file. The following information must be logged onto this form:

1. Client and Log #s
2. Date/Time Unpacked
3. Logged In/Numbered By (Initials)
4. 2nd Checked By (Initials)
5. Date/Time Placed in Cold Storage
6. Storage Area (Walk In, Hobart-VOCs, Quarantined Soils, Quarantined-VOC, Other)
7. Disposed of By/Date
8. Method of Disposal

E. Notify the proper analyst if samples have been logged in for analyses which have a 24-48 hour holding time or if a 1-2 day turnaround has been requested. The log number and description on sample (s) must be second checked before it is released to the analyst. (The analyst can second check the sample, but must initial the custody form.)

III. Sample Storage

A. After samples have been correctly logged in they are then transferred to one of the following cold storage areas and arranged in numerical order by the assigned log in/LIMS sample number. ***Note that aqueous VOC samples must be segregated from all other samples.***

1. The Blue Air refrigerator in Sample Storage Room: All aqueous VOC's must be stored in this refrigerator. Storage blanks consisting of organic free water from the laboratory may

be required for specific projects. These will be analyzed for VOCs only. ***Storage blanks are required for all CH2M Hill and AFCEE projects.***

2. Walk In Refrigerator in Sample Storage Room: All aqueous samples for all analyses must be stored in this refrigerator

3. Soil Walk-In Refrigerator in back BC Laboratory: All quarantined and non-quarantined soil samples for all analyses must be stored in this refrigerator.

B. Quarantined soils are those quarantined by the US Department of Agriculture. These soil samples must be segregated from other soil samples during storage. A separate disposal log must be maintained for these soils including the location, date and quantity of the soil received and processed. Soil residues from quarantined samples must be treated according to regulations after testing (see Sample Disposal SOP). Quarantined soils are defined as:

1. Soil taken from much of the southeastern US and parts of New York and Maryland at a depth of three feet or less. *Soils from three feet or more are not regulated provided they are stored separately.* A map of the regulated areas in the United States entitled ***Soil Movement Regulations [Attachment VIII]*** is posted in the log-in room.

2. All soils taken from foreign sources, US. territories and Hawaii .

NOTE: All soils are treated as quarantined soils and are disposed of in accordance with USDA regulations. Above for information purposes only.

C. All samples must be stored in one of the three refrigerators detailed above with the following exceptions:

1. Matrices that may be adversely affected by the cold temperature. (e.g. surfactant samples, multi-phase samples)

2. Highly contaminated waste or product type samples that could jeopardize the integrity of other samples in the walk in cooler. Often these can be stored at room temperature. If these require refrigeration see the Project Manager for other options.

D. The temperature of each sample refrigerator must be monitored and recorded each day by Wet Chem personnel by the following method. A Mercury thermometer or digital min/max thermometer with 1° increments must be used. Each thermometer must be calibrated against a NIST certified thermometer once a year**(digital thermometers quarterly)** and this information recorded in a bound notebook. The Certificate of Calibration for the NIST thermometer is kept on file at the QAO's desk. The thermometers must be tagged with a unique identification, the date calibrated and the correction factor.

The tolerance range for all refrigerators is 1 to 6°C. This range and the range using the corrected reading must be posted on the outside of each cooler. If the temperature exceeds this range,

corrective action measures must be put in place immediately. A CAR must be completed specifically noting the date and time the problem was discovered. The Project Manager, Laboratory Director and Technical Director will be notified in order to assess the situation. It may be necessary to put a service call in to the refrigeration repair service.

E. All personnel removing samples from any refrigerator must sign them in and out. This is done by completing the ***Sample Custody Form [Attachment IX]*** which is attached to the door of each refrigerator. These completed forms are kept on file [see section III, #4F]

F. The water walk in refrigerator in the sample room is the largest refrigerator and stores a large majority of the samples. A back up compressor is hooked into the system and scheduled to automatically come on if the main compressor fails. There is a digital min/max thermometer, which monitors the temperature 7 days a week. This thermometer will be calibrated quarterly against the NIST thermometer.

G. As stated above the temperatures for all refrigerators that samples are stored are checked each day Monday-Friday and monitored seven days a week with min/max thermometers. Pay close attention to these readings and watch for signs of possible problems.

H. A temperature maintenance record book is kept for each refrigerator.

I. Samples must be held for a minimum of 30 days after the final report unless specified otherwise. For USACE projects, samples must be held for a minimum of 60 days after the final report unless otherwise specified. See SOP ATSD 405 entitled Analytical Laboratory Waste Disposal SOP for guidance on disposal of samples.

IV. Laboratory Information Management System (LIMS)

A. Log the sample information into the LIMS for each sample. Every attempt should be made to get every sample logged into the LIMS by the end of the day. All information should be clearly stated. Note: the work-order number (w.o.#) can be assigned prior to entering all sample information. Make sure the w.o.# number is recorded on the chain of custody to help. After opening the main menu of the LIMS click on WORKORDERS and then click on ADD to create a new workorder. You will see the following:

1. ***Client I.D.*:**

   Select the client I.D. by clicking on the pull-down and choosing from the client list. This list is not always in alphabetical order. If the desired client is not on the list, a new client must be created (See OMEGA LIMS handbook).

2. ***Project I.D.*:**

Click on project and choose the project I.D. The projects will be client specific. After the project is chosen the "project information" area should fill in. The "project name", "QC level", "TAT", and "Report to" information should also appear. If there are no project choices, a project must be created (See OMEGA LIMS handbook). There are two types of projects:

a. Internal—Empirical Laboratories projects; use job/task #

b. External--direct laboratory clients; use X------- where the last two spaces are a counter. Example: XMONWW01

[Pay close attention as a few clients are actually both.]

3. ***Comments:***

Record any additional comments or observations. This includes but is not limited to information concerning rush turnaround, deliverables or other QC requirements, analyte concentrations, safety issues, quarantined soils, CAR #s, preservation or matrix problems, etc.

4. ***Rec. by:***

Enter the initials of the person who received the samples.

5. ***Received:***

Enter the date and time received separated by a space and using military time.
Example: 1/1/02 16:30

6. ***Date Due:***

After the date and time received have been entered, tab down to date due and this date will be calculated.

7. ***Coolers:***

Click on "Coolers" tab and enter temperature on receipt.

8. ***Invoice Info:***

a. Click on the Invoice Info. tab and enter any discount or surcharge
b. Add the purchase order number when applicable. A listing of yearly/blanket PO #'s is posted in the log in room. This is periodically updated by the Project Manager.

After these items have been completed, click on the Login button to continue.

9. ***Client Sample I.D.:***

   a. Only abbreviate if description is too long for the spaces allotted in the LIMS or on the computer tracking logs. This information should come directly from the chain of custody. The sample ID entered into the LIMS will be the sample ID on the final report.

   b. Include date as part of the description if this is the only way to differentiate the samples. This should always be done with certain clients who have requested it and may be necessary for samples received from the wastewater treatability laboratory.

   c. When logging in trip blanks for VOA list them as "Trip Blank # _____". This information should be on the containers. A log book must be kept in the sample kit room which lists all trip blanks and the date they were filled. This will ensure consistency with the descriptions for trip blanks. Make sure you record the trip blank on the chain of custody if it is not listed.

10. ***Collection Date:***

    Enter the date and time the sample was collected. You must use military time and separate by a space. Often the time collected is not given. Although this is a sampling requirement, this information may not be crucial unless a parameter with a short holding time or a data deliverables package is required. All attempts should be made to get all our clients to supply this information.

11. ***Matrix:***

    Click on pull down and select matrix. Many times it is difficult to select the matrix and log-in personnel must use their best judgment. Keep in mind that the detection limits and units on the LIMS reports are linked to the matrix. In some cases it may be necessary to ask the Section Managers about the matrix selection.

12. ***Bottle Type:***

    Click on the pull down and select the appropriate bottle type.

13. ***# Containers:***

    Enter # of containers of the same bottle type.

14. ***COC ID:***

Enter this number for USACE and other specified projects.

15. ***Comments:***

Enter any information that is applicable at the sample level.

16. ***Field Data:***

Click on field data tab and enter field information.

Sampler: Enter in the sampler's initials. If this information is not available leave this section blank or record NG for not given. This information should be given, however it may not be crucial. All attempts should be made to get all our clients to supply this information.

a. pH: Enter the field pH

b. Site Type: Enter F for "field" pH
c. Enter R for "lab" pH

d. **Technique**: Enter sample type (grab or composite)

17. ***Tests:***

a. Click on the box below Tests and then click on the pull-down. Select parameters from this list.

b. Pay close attention when selecting the analyses, as more than one method may be listed in the LIMS directory for each type of analyses. A few examples of these are: TPH, VOA, Ammonia, Oil and Grease, Phenol and Metals. Do not guess at the method. If the method is not known, take the time to ask before selecting it in the LIMS. If only specific organic analytes are requested this information must be forwarded to the Organic Manager.

c. For NPDES samples note the following requirements: A list of ***Routine NPDES clients [Attachment XI]*** is posted in the Sample Receiving Room. This is only a guide and should not be considered absolute. Always ask if you are ever in doubt. Remember that some clients may send in samples for NPDES monitoring and RCRA monitoring, etc.

1. Samples that require Ammonia analysis must be logged in and analyzed by the distillation method. This is per 40 CFR 136 that states that "Manual

distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary." If we choose to do this for any client, this information must be documented and kept on file. It is the responsibility of the Inorganic Manager to track this information and inform the sample receiving group of any clients that may fall into this group.

2. All NPDES samples that require organic analyses must be logged in for 600 series methods (608 for Pest/PCB, 601/602 or 624 for VOA and 625 for BNA). Samples from RCRA projects that require organic analyses must be logged in for SW-846 methods (8081/8082 for Pest/PCB, 8260 for VOA and 8270 for BNA.)

   a. Non aqueous samples for organic analyses must list an extraction method; low vs. medium and sonication vs. soxhlet.

   b. For most non-aqueous samples, it will be necessary to log the sample in for % solids in order for the sample result to be reported on a dry weight basis. The general rule of thumb is that all soil and sediment samples will be reported on a dry weight basis unless otherwise requested from the client. Separate LIMS codes are set up for the Metals analyses (soil vs. soil dry weight.)

   c. It may be necessary to add in additional non testing codes such as sample kits, labor hours, mileage, ISCO rental, QC requirements, etc. for billing purposes. You can add these while adding analytical tests.

If bottles are received that are the same sample volume but have different preservatives but you must "add fractions".

18. ***Add Fraction:***

To add a fraction click on the "Add Fraction" button. The cursor will take you back to step 12. From here you may proceed to enter additional sample containers and associated parameters.

19. ***Add Sample:***

Click on the "Add Sample" button to add a sample within the same workorder. The cursor will return to step nine where you may enter the next sample.

Once all the tests have been selected and all samples have been added in the workorder, login of this group of samples is complete.

V. Daily Follow Up for Sample Receiving/Log In

A. Wipe out the inside of coolers and return all Empirical Laboratories coolers to the sample kit room. Discard any coolers that are cracked, broken or filthy.

B. Complete the short holding times log book as required. This must be done as early in the day as possible.

C. If any samples were received for RUSH turnaround, then a ***RUSH SHEET [Attachment XII]*** must be completed and distributed to all laboratory personnel via e-mail. If ever in doubt of which analysts should be notified, pass them out to everyone. Always give copies to the Laboratory Director, Administrative Assistant and Section Managers. It may be necessary to send out two RUSH sheets per day (one around mid-day and the other at the end of the day).

D. Complete any required CARs.

E. At the end of the day organize all paperwork received and generated for the day . The following should be given to the Project Manager (section supervisor):

1. The original chain of custodies and yellow original or copy of each.

2. Any information (letters, regulatory limits, etc.) from a client which was received with any samples.

3. All CARs.

4. LIMS sample receiving logs.

5. Copies of any RUSH sheets which have been distributed

6. Sample Receiving Custody and Disposal Form.

7. Cooler receipt form if required.

G. All the above information from the day will be reviewed as soon as possible.

1. All LIMS logs must be 2nd checked by a different person than the person entering the information into the LIMS. Each set of logs must be initialed dated by the person 2nd checking. These will be kept on file at the Project Manager desk.

2. If any corrections or changes are required, all laboratory personnel will be notified by distributing a ***Sample Log Change Form [Attachment XIII]*** through email distribution.

A ***Sample Log Change Form*** by the project manager will also be sent out if a client adds or deletes any parameters, changes sample IDs, etc.

H. The Testing Coordinator will distribute the following (on a daily basis if possible) after they have been through the 2nd QA check:

1. Copies of the LIMS receiving reports to necessary laboratory personnel.

2. Original (white copy) chain of custodies are given to the Project Manager. These will be sent with the final report to the client.

3. Finalized/approved CARs must be sent to the:

   a. Organic Manager

   b. Inorganic Manager

   c. Laboratory Manager

   d. Laboratory Director {optional}

   e. Quality Assurance Officer

   f. Administrative Assistant

   g. Client {optional}

4. Copies of any project/sample specific information to the Section Manager and analysts.

I. Information will be filed as follows:

1. Chain of custodies:

   a. Original (white copy) are returned to the customer with the final report.

   b. Yellow copy originals or photo copies will be filed by client and kept in the Sample Receiving Room.

   c. Photo copies will be kept in a notebook in numerical order in the Sample Receiving Room.

   d. Pink copies should be retained by the sampler.

2. CARs

a. CARs can be found at V:\LAB\log-in\login(year)\logcar(year).

3. Sample Change Forms and RUSH Sheets

a. Sample Change Forms are distributed by email.

b. RUSH Sheets are found at V:\LAB\login\Rushsheets

4. At the end of each year, files for that year are boxed and archived. Make sure files are labeled properly and place them in banker's boxes. Complete a storage box file form with as much detailed information as possible. The Laboratory Administrative Assistant will label and number the boxes and incorporate the storage boxes into the laboratory file archive system. Boxes containing files from Sample Receiving are kept on site for 1-2 years and then may be moved to off site storage upon release from the Project Manager.

VI. Miscellaneous

A. All projects which require deliverables or other QC requirements should be listed in the notes section of the LIMS.

B. If samples are received from a new client or a new job number that is not in the LIMS, a new client code must be set up. This information should be on the chain of custody or it may be necessary to contact the customer if the information is incomplete.

C. Samples from the Aquatic Toxicity Laboratory (ATL) are logged into the LIMS for billing and long-term tracking purposes. The receiving information and proper assignment of test's are reviewed by the ATL Manager. The samples are then logged in by ATL personnel.

D. A flow chart outlining sample receiving and the flow of data, reporting and invoicing is attached as ***Attachment XIV.***

E. A ***Telephone Conversation Log [Attachment XV]*** may be required to document information and may be attached to or used as a CAR.

F. All log books used in the Sample Receiving and Sample Storage Areas are numbered. The following log books are presently maintained. All log books must be "Z"ed out. The Testing Coordinator will review the log books each week to check for completeness.

Log Book ID	**Log Book Description**
SRLB #3	pH Paper Calibration
SRLB #4	Tracking of VOC Trip Blanks, Organic Free Water and Chemical Preservation

Attachments to SOP 404

II	Chain of Custody Record
III	Corrective Action Report for Sample Receiving/Log In
IV	Cooler Receipt Form (used for USACE project)
V	List of Short Holding Time (Immediate-72 hrs.) Parameters
VII	Sample Receiving Custody and Disposal Form
VIII	Map of Quarantined Soil Areas in the US.
IX	Laboratory Sample Custody Form for Walk In Refrigerator
X	Container Codes for the LIMS
XI	Routine NPDES Clients
XII	RUSH Sheet
XIII	Sample Log Change Form (Green Sheet)
XIV	Flow Chart, Laboratory Sample Tracking System

[Attachments I and VI were removed during the editing process and not added to the SOP.]

ANALYTICAL LABORATORY WASTE DISPOSAL

SOP NUMBER: **SOP-405**

REVISION NUMBER: **4**

APPROVED BY:

TECHNICAL DIRECTOR

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: **09/26/03**

DATE OF LAST REVIEW: **04/23/08**

Analytical Laboratory Waste Disposal
Standard Operating Procedure

I. SCOPE AND APPLICATION:

Empirical Laboratories, LLC laboratory waste includes excess client sample waste and waste that are generated while performing an array of analytical services, some of which are hazardous. These wastes must be disposed of in a manner that is safe, cost efficient and in accordance with hazardous waste regulations.

A. Wastes can be broken down into the following categories:

1. Unused portions of actual samples received from outside clients.

   a. Unused aliquots of completed water samples.

   b. Unused aliquots of completed non-aqueous samples.

2. Soils from quarantined areas

3. All other soils, sediments, building debris, wipes etc.

4. Hazardous waste generated within the laboratory as part of numerous analytical procedures.

II. SUMMARY OF PROCEDURES:

A. There are four options for disposing of unused sample portions:

1. Return completed samples and any generated waste from these samples to the client.

2. Throw the sample away after confirming that it is non-hazardous.

3. Disposal through a waste vendor in either a sealed drum or lab pack. This is normally done twice a year.

4. Treat the sample to make it non-hazardous and dispose of it as such. (Aqueous pH neutralization only.)

B. There are two options for disposing of laboratory generated waste:

1. Disposal through a waste vendor in either a sealed drum or lab pack. This is normally done twice a year. The waste must be stored properly until the waste is transported off site.

For example: Solvent waste must be stored in the vented flammable cabinet.

2. Treat the waste to make it non-hazardous and dispose of it as such. (Aqueous pH neutralization only.)

III. EQUIPMENT/APPARATUS:

A. Proper safety equipment in good working condition. This includes gloves, lab coat and safety glasses/goggles (voluntary use of cartridge respirator allowed see area manager or QAO).

B. USDOT approved drums for storing and shipping hazardous waste.

C. Fume hood vented outside the building.

D. Flammable storage cabinet which is vented to the outside

IV. PROCEDURE

Waste disposal is done under the management and coordination of the Sample Receiving Manager, Section Managers and the Health and Safety Officer.

A. Disposal of completed aqueous samples:

Completed samples are kept in cold storage for approximately three weeks after the final report has been mailed. Engineering support projects involving CLP work, litigation cases etc. may be saved for longer than three weeks at the request of the project manager.

No samples should be disposed of without approval from the responsible area manager or analyst. **At this point the area manager and/or analyst will communicate information about samples deemed as hazardous**.

1. The majority of the water samples (ground, surface and drinking) are non-hazardous and are disposed of by pouring them down the sink.

a. This must be done under the hooded area located near the walk in cooler next to the extraction lab. Make sure that the sash is closed far enough to produce sufficient ventilation. The tap water should be turned on to supply copious wash for sample disposal.

b. Proper safety equipment **must** be used including safety glasses (face shield if necessary), lab coat and gloves.

c. **Be alert to potential problems: for example, separate Cyanide waste from acid waste. Neutralize acid waste that will be poured down the acid drain and don't mix waste/samples thought to contain Cyanide with samples that are acidified. Also, look for things such as phase separation, odd color, odor etc. Check with the area manager or Health and Safety Officer before disposing of any questionable samples.**

d. Tap water must be running during the time samples are poured out and for approximately 10 minutes after so sufficient flushing and dilution takes place.

e. All containers must be rinsed out, all identifying markings defaced or removed, and thrown into the trash.

f. All samples disposed of in this manner must be documented in the bound disposal log.

2. If water samples are hazardous (known or suspected), one of the following steps must be taken.

a. Samples may be returned to the client. If you plan to ship the unused portion back to the client check with shipping and receiving to make sure that the material can be shipped in accordance with USDOT regulations. **If the samples are not returned to the client they must be stored properly until picked up by a waste vender.**

b. Treat the sample to make it non-hazardous. One example of this is if the sample is highly corrosive, the pH may be adjusted.

c. Store the sample properly until either a sealed drum or lab pack is sent out.

d. All samples disposed of in this manner must be documented in the bound disposal log.

B. Disposal of completed non-aqueous samples:

The majority of non-aqueous samples are soils or sediments, although there may also be building debris, wipes, oils**,** and occasionally product type samples.

1. If samples are non-hazardous they must have all identifying markings defaced or removed, and thrown into the trash. On specific projects we may also opt to return the unused portions to the client even if they are non-hazardous.

2. If non-aqueous samples are hazardous (known or suspected), one of the following steps must be taken.

a. Samples may be returned to the client. If you plan to ship the unused portion back to the client check with shipping and receiving to make sure that the material can be shipped in accordance with USDOT regulations**. If the samples are not returned to the client they must be stored properly until picked up by a waste vender.**

b. Store the sample properly until a lab pack is sent out.

3. Soil samples taken at a depth of three feet or less from areas, which have been quarantined by the US Department of Agriculture (USDA), must first be treated at the laboratory to prevent the spread of any plant pests. The USDA has detailed proper treatment procedures of which we use the following:

a. The sample is heated to 180°C(356°F)in a vented oven for one hour.
b. After the heating the samples are placed close to a hood to cool and are marked as being ready for disposal.

4. Once the samples have undergone treatment they can then be disposed of by one of the procedures for non-aqueous samples**. All samples disposed of in this**

manner must be documented in the bound disposal logbook with the following information:

a. Client
b. Sample #s
c. Date(s) treated
d. Treatment method used

C. Disposal of laboratory generated waste:

Generated waste is stored in satellite areas until a waste pick up occurs. These satellite areas must be maintained properly.

1. Waste handling and disposal within each laboratory section:

Each laboratory analyst and section manager is responsible to assure that **handling** operations within their area are being followed according to the laboratory requirement.

a. General Chemistry/Inorganic

Each analyst performining specific laboratory tests that generates waste is responsible to handle and dispose of the waste in a safe manner and under the guidelines listed below. If you have any questions left unanswered regarding waste disposal within your specific area contact the inorganic manager or the safety officer.

- Concentrated acid waste, **(>2% by volume) and** dilute mercury waste (mercury, chemical oxygen demand, total kjeldahl nitrogen and chloride analyses waste) are poured into the Acid Satellite Waste drum in the general chemistry laboratory. **Document the type and amount of waste in the acid waste logbook, then initial and date the entry**.
- Dilute acid waste **(<2% by volume or less)** are neutralized and poured down an acid drain with copious amounts of tap water.
- **All other non-hazardous sample waste, reagents and standards are poured down the drain with copious amounts of tap water.**

b. Metals

Each analyst performining specific laboratory tests that generates waste is responsible to handle and dispose of the waste in a safe manner and under the guidelines listed below. If you have any questions left unanswered regarding waste disposal within your specific area contact the inorganic manager or the safety officer.

- Concentrated acid waste, aqueous sample waste digestates and old unused calibration standards **(>2% by volume)** are poured into the Acid Satellite Waste drum in the general chemistry laboratory.
- Non-aqueous sample digestate wastes are decanted off the soil/solid samples into the Acid Satellite Waste drum in the General Chemistry Laboratory. **Rinse the soil/solid with tap water several times and discard the first rinsate into the Acid Satellite Waste drum and the sequential rinsates decant down an acid drain with copious amounts of tap-water.**
- **Throw the soil/solids in the trash once the acid has been rinsed free**.
- **Cr6 digestates as with all concentrated metal/acid waste are poured into the Acid Satellite Waste drum.**

c. Organic Extraction Laboratory Area

Each analyst performining specific laboratory tests that generates waste is responsible to handle and dispose of the waste in a safe manner and under the guidelines listed below. If you have any questions left unanswered regarding waste disposal within your specific area contact the organic manager or the safety officer.

- Concentrated acid waste is discarded into the Acid Satellite Waste drum in the General Chemistry Laboratory.
- Non-chlorinated solvent waste (Acetone, Ether, Hexane, Methanol ….etc…) pour into the Non-Chlorinated Waste labeled bottle located in the hood in the Organic Extraction Laboratory.
- Chlorinated solvent waste (Methylene Chloride, Chloroform, chlorinated standard and spike waste) pour into the Chlorinated Waste labeled bottle located in the hood in the Organic Extraction Laboratory.

****Note: Laboratory generated solvent waste is transferred to the appropriate Satellite Solvent Waste Drum (chlorinated or non-chlorinated) weekly or as deemed necessary. Disposal of solvent waste is done under the direction of the organic laboratory manager. These drums are located in the chemical reagent storage room and only authorized laboratory staff are allowed to add waste solvent to these drums. The date of addition to the**

drum , type and quantity of solvent is entered into the '*Organic Solvent Waste Logbook*' located on the shelf next to the drums.

- **Aqueous sample waste from extracted samples (once the extraction solvent has been removed) is poured down the drain and flush with copious amount of tap water.**
- Non-aqueous sample waste and sodium sulfate waste is dumped into a waste container under an extraction laboratory hood and left overnight or until the solvent is evaporated and then the waste is discarded into the trash.

d. Gas Chromatography (GC)/High Performance Liquid Chromatography (HPLC) Laboratory

- Autosampler vials are discarded into the appropriately labeled box located under the table in the GC/HPLC Laboratory.

PCB Box – all samples/standards
Pesticide Box – all samples/standards
Herbicide Box – all samples/standards
8330 Box – all samples/standards
Methylene Chloride Box- all samples/standards that contain methylene chloride (Diesel Range Organics, DRO)

- Sample and spike extract vials are separated according to the contents in the vial.

Acid cleaned extracts are combined into a separatory funnel and the acid layer separated from the solvent. The acid portion is discarded into the Acid Satellite Waste drum in the general chemistry laboratory. The solvent waste is discarded into the appropriate solvent waste bottle (chlorinated/non-chlorinated waste) located in the hood in the organic extraction laboratory.

After the mercury has been recovered from the mercury cleaned samples, the extracts are discarded into the proper waste solvent bottle (chlorinated/non-chlorinated waste) in the hood in the organic extraction laboratory. The mercury waste is consolidated and discarded into the mercury waste container located in the vented hood in the chemical storage room. **Mercury used for removing sulfur from samples has been discontinued in our laboratory**.

Unused stock and working standards are discarded into the chlorinated solvent waste bottle located in the organic extraction laboratory. The empty vials are rinsed

several (3) times with solvent and the solvent rinsate poured into the solvent waste and the vials with labels removed are discarded into the glassware waste container.

e. Gas Chromatography/Mass Spectrometry

- Volatile sample, standard and reagent waste

Waste from the instrument - Aqueous sample waste is collected in waste bottles via waste lines from the instrument. The bottles are emptied into buckets and poured down the drain(pH is < 2% by volume). A small amount of methanol used to clean glassware is also dumped into the bucket and poured down the drain. While disposing of sample waste always run the cold tap water 10-15 minutes. Non-aqueous waste from sample analyses is retained and dispose of in the samey as the unused sample. Unused sample is held for sample disposal by the sample receiving area, see A and B listed above.

Standards - **Unused stock and working standards** are discarded into the chlorinated solvent waste bottle located in the organic extraction laboratory. The empty vials are rinsed several (3) times with solvent and the solvent rinsate poured into the solvent waste and the vials with labels removed are discarded into the glassware waste container.

In conjunction with section managers, the sample receiving area disposes of solid sample waste and unused aqueous and solid samples, see procedures A and B listed above.

- Semivolatile sample and standard waste disposal

Methylene chloride waste solvent and standard waste in vials are poured into the chlorinated waste bottle in the hood in the organic extraction laboratory. The empty vials are rinsed with solvent and the solvent poured into the waste solvent bottle. The vials with labels removed are discarded into the glassware waste disposal container.

Auto sampler vials are collected in buckets and stored under the hood in the organic extraction laboratory. **Periodically the vials are consolidated in lab packs for disposal by a licensed waste disposal company**.

f. Bioassay Laboratory

- Aqueous sample waste and a small amount of methanol are poured down the drain with copious amounts of tap water. Larger amounts of methanol used for glassware cleaning are collected in beakers and evaporated at room temperature.

- Hazardous or product samples are returned to the client.

D. Consolidation of satellite waste for contractor disposal:

In conjunction with the Safety Officer, the sample revieving supervisor is responsible to coordinate waste disposal operations with outside waste disposal contractors.

1. Solvent waste from the areas discussed above is periodically consolidated into two drums located in the Chemical Storage room (c. *Organic Extraction Laboratory Area*, *** Note**). A drum designated either chlorinated or non-chlorinated solvent waste is available to receive the appropriate solvent waste. When the drums become full (fluid surface six inches below the top of the drum), an authorized hazardous waste contractor will be scheduled to remove them to proper waste disposal.

2. The Acid Satellite Waste drum is also disposed through the authorized hazardous waste contractor once the drum is full to the level of six inches below the top of the drum.

3. Consolidated autosampler and standard vials are periodically Lab-Packed in drums and disposed through the authorized hazardous waste contractor.

4. The Laboratory Health and Safety Officer will administer the Waste Disposal Program and maintain current information to track quantities of waste generated and stored on-site.

It is the continuous objective of our laboratory to find ways to decrease the amount of waste generated.

STANDARD OPERATING PROCEDURE (SOP) FOR LABORATORY SAMPLE STORAGE, SECURE AREAS AND SAMPLE CUSTODY

SOP NUMBER: **SOP-410**

REVISION NUMBER: **5**

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: **06/18/08**

DATE OF LAST REVIEW: **06/18/08**

STANDARD OPERATING PROCEDURE (SOP) FOR LABORATORY SAMPLE STORAGE, SECURE AREAS AND SAMPLE CUSTODY

Empirical Laboratories, LLC is located on the fifth floor of a building which is locked and monitored by a guard after normal business hours. No unauthorized personnel are permitted within the facility without a proper escort and a visitor's badge. During non business hours, all doors to the building are locked and the elevators are security coded (i.e. a code must be entered in order to get the elevator to open on the fifth floor.) All stairway doors are locked and only Empirical Laboratories, LLC personnel have a key to the fifth floor stairway door. The doors to the lab in the hallway have a key code. There is a buzzer at the door to Login to allow entry for sample and supply deliveries.

The majority of samples are shipped in coolers by couriers such as Federal Express and UPS. All couriers are generally received in the Shipping/Sample Receiving (SR) area on the fifth floor. The laboratory is located close to Federal Express (FedEx) distribution station, therefore we pick up our coolers at the FedEx location on Saturdays and transport them directly to the laboratory. Some coolers and/or samples are delivered directly to the SR area by the sampler and/or client. The SR personnel must not leave any packages/cooler without authorized receipt from laboratory personnel. Samples must be accompanied by some type of chain of custody record. Sample receiving personnel sign, and list the date and time received on the chain of custody. The time received must reflect the actual time or validation date and time of receipt for the samples although they may be placed in cold storage and logged into the system at a later time. The method of delivery is listed on the chain of custody. A copy of the airbill (if available) is attached to the chain of custody.

Once sample containers have been assigned a laboratory ID number, they must be checked by another laboratory individual to ensure that the log number on the container matches the log number and sample ID on the Chain of Custody. A Sample Receiving Custody and Disposal Form (attached) must be completed each day. Samples should not leave the log-in area until this has been completed. A copy of this form must be given to the Testing Coordinator at the end of the day. The original is to remain in Sample Receiving until the samples are disposed. Once the document

is complete, the original will be kept on file. The following information must be logged onto this form:

- Client and Log #s
- Date/Time Unpacked
- Logged In/Numbered By (Initials)
- 2nd Checked By (Initials)
- Date/Time Placed in Cold Storage
- Storage Area (Walk In, Hobart-VOCs, Quarantined Soils, Quarantined-VOC, Other)
- Disposed of By/Date
- Method of Disposal

Original samples are stored in following areas of the fifth floor. The Water Sample Storage and Sample Receiving rooms are locked during non business hours. Only laboratory personnel have keys to these areas.

1. Hobart Refrigerator in Sample Storage Room: All water VOCs must be stored in the refrigerator.

2. Walk In Refrigerator in Sample Storage Room: All waters for all analyses except VOCs must be stored in this refrigerator.

4. Soil Walkin Refrigerator for all soils.

All soils are treated as quarantined.

All samples must be stored in one of the three refrigerators detailed above with the following exceptions:

1. Matrices that may be adversely affected by the cold temperature. (e.g. surfactant samples, multi-phase samples)

2. Highly contaminated waste or product type samples which could jeopardize the integrity of other samples in the walk in cooler. Often these can be stored

at room temperature. If these require refrigeration see the Testing Coordinator for other options.

Any person removing samples from the storage areas listed above, must sign them out on a laboratory custody sheet (attached). The individual performing the processing becomes responsible for the samples at this point. The samples are maintained in the secure possession of the individual processing the samples. When the processing is completed, the samples are returned and signed back into the appropriate storage area. It must be noted if the entire sample volume was used and that the container was discarded.

Sample extracts and digestates are stored in the following areas:

1. All metals digestates are stored in the metals instrument laboratory. The transfer from the digestion analysts to the ICAP analysts is documented in the metals digestion log book.

2. Non ZHE TCLP extracts are returned to the refrigerator in which the original samples are stored. For ZHE samples, the extract is returned to the refrigerator in which the original VOC sample containers are stored.

3. Extracts from medium level VOC analyses are also stored in the VOC sample refrigerator.

4. All Organic extracts for are stored in a "Hobart" side by side refrigerator in the organic extraction laboratory.

The generation of all sample extracts/digests and their movement through the laboratory will also be tracked on a laboratory custody sheet or in a log book. The individual performing the processing becomes responsible for the samples at this point. The samples are maintained in the secure possession of the individual processing the samples. When the processing is completed, the extracts are returned and signed back into the appropriate storage area. The metals digestates are not removed from the metals instrument laboratory.

After the analytical results have been reported, the original samples, sample extracts, and digestates will remain in secure storage until they are disposed of in accordance with the Waste Disposal Standard Operating Procedure. Samples will be held for a

minimum of 30 days after the final report unless specified otherwise. Sample extracts and digestates are held for a minimum of 60 days after the final report unless project specific requirements state otherwise. See SOP No. 405 entitled Laboratory Waste Disposal SOP for guidance on disposal of samples.

The following personnel as of February 10, 2006 have access to all sample storage areas:

Ashley Bester	Herbie Johnson
Roger Burr	Dahae Kim
Tanisha Custer	Dustin Lynch
Rick Davis	Marcia McGinnity
Barbara Dawson	AntonioMontiero
Betty DeVille	Ashley Morris
Amanda Fei	E. J. Overby
Kendra Gentry	Kevin Perzynski
Sonya Gordon	Brenton Powers
Gwen Hallquist	Brian Richard
Andrew Holder	Franklin Rivers
Jade Holliman	William Schwab
John Hughes	Rebecca Sherman
Karu Huka	Ted Taylor
	Christy Thompson
	Renee Vogel
	Randy Ward

In the event that an employee is terminated, the supervisor is responsible for collecting the employee's keys.

For additional information see SOP No. 404 entitled Laboratory Sample Receiving, Log-In and Storage.

Title: CATION ION EXCHANGE CAPACITY OF SOILS (SODIUM ACETATE) SW-846 Method 9081

Approvals (Signature/Date):

4-16-08
Rodney Street — Date
Department Supervisor

4-15-08
Michael H. Dunn — Date
Technical Director

4-30-08
Jared Knierim — Date
Health & Safety Manager / Coordinator

4/28/08
Eric S. Smith — Date
Quality Assurance Director

4-29-08
Johnny A. Mitchell — Date
Laboratory Director

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Facility Distribution No. 06-91 **Distributed To: QA Server, QA, M, 06**

1.0 Scope and Application

1.1 Analyte, Matrices: This method is applicable to most soils, including calcareous and non-calcareous soils.

1.2 Reporting Limits: The typical laboratory RL is 1 meq/100g.

1.3 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 20 in the Quality Assurance Manual.

1.4 If for any reason a part of this SOP cannot be followed, seek the guidance of the Department Supervisor or the Laboratory Technical Director. All abnormalities must be noted on the data or the benchsheet, in the Non-conformance database, and in LIMS. See the corrective action procedures and Appendix 4 in the QA Manual.

2.0 Summary of Method

This soil sample is mixed with an excess of Sodium acetate solution resulting in an exchange of the Sodium cations for the other matrix cations. Subsequently, the sample is washed with Isopropyl alcohol. An Ammonium acetate solution is then added, which replaces the adsorbed Sodium with Ammonium. The concentration of displaced Sodium is then determined by optical emission spectroscopy.

3.0 Definitions

See TestAmerica Nashville's QA Manual Appendix 5 for laboratory definitions.

4.0 Interferences

Interferences can occur during analysis of the extract for sodium content. Thoroughly investigate the chosen analytical method for potential interferences.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements: None.

5.2 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetic Acid	Corrosive Poison Flammable	10 ppm-TWA	Contact with concentrated solution may cause serious damage to the skin and eyes. Inhalation of concentrated vapors may cause serious damage to the lining of the nose, throat, and lungs. Breathing difficulties may occur.

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Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Isopropanol	Flammable	400 ppm-TWA	Flammable liquid and vapor. Harmful if swallowed or inhaled. Causes irritation to eyes and respiratory tract. Affects central nervous system. May be harmful if absorbed through skin. May cause irritation to skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Mechanical shaker.
- Analytical balance, capable to 0.0001 g.

6.2 Supplies

- Volumetric flasks, Class A.
- Centrifuge tubes and caps, 50-mL, plastic.
- Graduated cylinders, Class A.
- Plastic vials, 100-mL, graduated, with caps.
- pH test strips.
- Teflon™ boiling chips.

7.0 Reagents and Standards

7.1 **Reagent water**, analyte-free, ASTM Type II or equivalent.

7.2 Sodium Acetate (NaOAc), 1.0 N: Dissolve 136 g of $NaC_2H_2O_2*3H_2O$ in reagent water and dilute it to 1,000 mL. The pH of this solution should be 8.2 ± 0.05. If needed, add a few drops of Acetic Acid or NaOH solution to bring the solution to pH 8.2. Record the pH.

7.3 Ammonium Acetate (NH_4OAc), 1 N: Dilute 57 mL of glacial Acetic Acid (99.5%) with reagent water to a volume of approximately 500 mL. Then add 69 mL of concentrated Ammonium Hydroxide (NH_40H) and add reagent water to obtain a volume of about 980 mL. Check the pH of the resulting solution, add more NH_40H, as needed, to obtain a pH of 7 ± 0.05, and dilute the solution to a volume of 1 liter with reagent water. Record the pH.

7.4 Isopropyl alcohol: 99%, commercially purchased.

7.5 Sodium Hydroxide, reagent grade (10 N commercial solution is acceptable.)

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Solid	HDPE or Glass	1-10 g	NA	6 months	SW-846 Chapter 2

Temperature preservation is not used. See the sample collection, preservation, handling, and storage sections of the Quality Assurance Manual.

9.0 Quality Control

Refer to the quality control section of TestAmerica-Nashville's QA Manual for specific quality

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control (QC) procedures. The laboratory maintains a formal quality assurance program and records to document the quality of the data generated.

9.1 Sample QC - The following quality control samples are prepared with each batch of **no more than 10 samples.**

Quality Controls	Frequency	Control Limit	Corrective Action
Method Blank (MB)	1 in 10 or fewer samples	< Report Limit	Correct problem, then reprep and analyze the LCS, all sample, and QC in the affected analytical batch.
Sample Duplicate	1 in 10 or fewer samples	<20% RPD	Report

- **Laboratory method or preparation blank (MB/PB)** - The laboratory prepares and analyzes at least one MB with each batch. MB data are used to assess contamination from the laboratory environment. MB values that exceed the MDL indicate laboratory or reagent contamination should be suspected. The source of the contamination must be determined and corrected and acceptable MB values must be obtained. Use the A mmonium acetate solution and Teflon™ boiling chips.
- A **Laboratory Control Sample (LCS)** – At the time of the writing of this SOP, no material of known cation exchange capacity is available.
- **Sample Duplicate** – Duplicate 1 in 10 samples for this analysis. Attempt to obtain a heterogeneous sample so that each aliquot is as identical as possible.

9.2 Instrument QC: See SOP 6010 / NV06-44 for instrument QC.

10.0 Procedure

10.1 Sample Preparation

Matrix	Sample Size
Solid	4 gram

Weigh 4 ± 0.1 g of medium- or fine-textured soil or 6 ± 0.1 g of coarse-textured soil and transfer the sample to a 50-mL centrifuge tube. (A fine soil has >50% of the particles ≤ 0.074 mm, medium soil has >50% ≥ 0.425 mm, while a coarse soil has more than 50% of its particles ≥ 2 mm.) Record the soil weight used.

10.2 Calibration

See SOP 6010 / NV06-44.

10.3 Sample Analysis

10.3.1 Add 33 mL of 1.0 N NaOAc solution, cap the tube, shake it in a mechanical shaker for at least 5 minutes. Record the start and stop time.
10.3.2 Centrifuge until the supernatant liquid is clear. Decant and discard the liquid.
10.3.3 Repeat steps 10.3.1 and 10.3.2 three more times.
10.3.4 Add 33 ± 0.1 mL of 99% isopropyl alcohol, cap the tube, shake it in a mechanical shaker for at least 5 minutes. Record each start and stop time.
10.3.5 Centrifuge until the supernatant liquid is clear. Decant and discard the liquid.
10.3.6 Repeat steps 10.3.4 and 10.3.5 two more times.

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10.3.7 Add 33 ± 0.1 mL of NH_4OAc solution, cap the tube, shake it in a mechanical shaker for at least 5 minutes. Record each start and stop time.
10.3.8 Centrifuge until the supernatant liquid is clear. Decant the washing into a 100-mL volumetric flask.
10.3.9 Repeat steps 10.3.7 and 10.3.8 two more times.
10.3.10 Dilute the combined NH_4OAc washings to the 100-mL mark with Ammonium Acetate solution and determine the Sodium concentration by ICP Method 6010 / SA06-44.

10.4 Example Analysis Queue / Sequence
Not applicable.

11.0 Calculations / Data Reduction
11.1 Accuracy – Not applicable.
11.2 Precision (RPD)

$$\text{RPD} = \frac{\text{Absolute value (orig. sample value - dup. sample value)}}{\text{[(orig. sample value + dup. sample value)/2]}} \times 100$$

11.3 Sodium cation / sample (µg/g) = $\frac{Na^+ \text{ conc. from ICP (µg/mL)} \times \text{100 mL extract volume}}{\text{Weight of sample (g)}}$

- Convert µg/g to mg/100 g by dividing by 10.
- The atomic weight of sodium is 23 (meq/100 g of soil = mg of Na/23).
- Report as meq/100 g = (mg/100 g) divided by 23.

11.4 Also, see the section on data reduction in TestAmerica Nashville's QA Manual.

12.0 Method Performance
12.1 Method Detection Limit Study (MDL)
The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP Determination of Method Detection Limits / NV08-202. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capability
The laboratory demonstrates initial proficiency by generating data of acceptable accuracy and precision for target analyses in a clean matrix. The laboratory also repeats the operation whenever new staff is trained or significant changes in instrumentation are made and on an annual basis thereafter. See the training section of TestAmerica-Nashville's QA Manual and SOP Training / NV08-199 for information on how to accomplish this demonstration.

12.3 Training Requirements

Demonstration of Capability is performed initially when learning the method and annually thereafter. Four Laboratory Control Samples resulting in an average % recovery within the control limits and a precision less than the quality control maximum are required.

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12.4 Proficiency Testing Studies

The laboratory participates in formal proficiency testing (PT) studies, where solutions of unknown concentrations are analyzed and the performance of all participants is compared. See the QA department for the results of recent PT studies.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i. e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / NV10-83.

15.0 References / Cross-References

15.1 SW-846 Methods 9081, Third Edition, September 1996.
15.2 TestAmerica Nashville's Quality Assurance Manual.
15.3 TestAmerica Nashville's Control Limits Manual.
15.4 SOPs: 6010 / NV06-44, Waste Disposal / NV10-83, Training Procedures for Environmental Technical Staff / NV08-199, Balance Calibration / NV08-213, Determination of Method Detection Limits / NV08-202.

16.0 Method Modifications

None.

17.0 Attachments

None.

18.0 Revision History

- Revision 4, dated 30 April 2008"
  - Integration of TestAmerica and STL operations.

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STANDARD OPERATING PROCEDURE

TestAmerica Analytical Testing Corp.
Nashville Division

Title: TNRCC Method 1005: TNRCC Method for Total Petroleum Hydrocarbons Characterization of C_6 to C_{35} Petroleum Hydrocarbons

SOP No.: TX1005 / SA04-157
Revision: 4
Effective: November 30, 2006

Computer File Name: TX1005-4

Supervisor Approval	10/30/06 Date		
Supervisor Approval	10-30-06 Date	Quality Assurance Approval	11/14/06 Date
Technical Approval	10-30-06 Date	Laboratory Director Approval	11-22-06 Date

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This method may involve hazardous materials, operations and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed toe, nonabsorbent shoes are a minimum. For specific hazard(s) see reagents, materials and procedure sections of this SOP.

Method Reference: TNRCC Method 1005, Revision 3 (Effective June 1, 2001)

Modifications:

Item	Method	Modification

Analyte: TPH C_6 to C_{12}, $>C_{12}$ to C_{28}, $>C_{28}$ to C_{35} and C_6 to C_{35}

Instrumentation: Gas Chromatography with Flame Ionization Detector

1 Scope and Applications

1.1 This gas chromatographic method is designed to determine the concentrations in solid or aqueous matrices of petroleum hydrocarbons from n-hexane (C_6) to n-pentatriacontane (C_{35}); an approximate boiling point range from 65°C to 499°C. This range includes gasoline, kerosene, diesel/fuel oil No. 2, some light lubricating oils and some portions of other heavier fuel oils and lubricating oils.

1.2 This method is a gas chromatography (GC) method with flame ionization (FID) as the mode of detection. The GC method is used to separate the TPH into three ranges (C_6 to C_{12}, >C_{12} to C_{28}, and >C_{28} to C_{35}).

1.3 The reporting limit is 50 milligrams/kilogram in solid matrix and 5 milligrams/liter in aqueous matrix.

1.4 This method is not intended for the quantitation of individual target analytes, such as benzene, toluene, ethylbenzene, and xylene (BETX) and polynuclear aromatic hydrocarbons (PAHs). Those target analytes are best determined by EPA Methods SW846 8260 / SA05-77, 8021 / SA05-90, and 8270 / SA04-22, where appropriate.

1.5 This method is used by, or under the supervision of, analysts experienced in the use of solvent extraction and gas chromatography. The analysts are also skilled in the interpretation of capillary gas chromatography data (specifically petroleum hydrocarbon pattern recognition), quantitation using computerized data acquisition, and use of peak processing software with baseline and peak grouping functions.

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2 Summary of Method

2.1 This method is a n-pentane extraction followed by gas chromatography with a flame ionization detector (GC-FID) analysis which measures the concentration of hydrocarbons between C_6 and C_{35}.

2.2 This method uses a 1:1 mixture of commercially available gasoline (unleaded) and diesel (#2 fuel) standard solutions as calibration standards and the n-alkane markers, C_6, C_{12}, C_{28} and C_{35} to establish the boiling point range boundaries.

3 Definitions

3.1 **Total Petroleum Hydrocarbons (TPH)** for the purposes of this procedure, total petroleum hydrocarbon is defined by the extraction procedure in this method and the area of all gas chromatographic peaks beginning with n-hexane (C_6) and ending with n-pentatriacontane (C_{35}).

3.2 **Locator Mix:** a mixture of C_6, C_{12}, C_{28} and C_{35} alkanes used to determine the C_6 to C_{12}, >C_{12} to C_{28} and >C_{28} to C_{35} boiling point ranges.

3.3 See the QA Manual QC section and Appendix 5 for additional definitions.

4 Interferences

4.1 Non-petroleum organic compounds which are soluble in n-pentane and which have boiling points in the range of interest can be measured under the conditions of this method; however, if present, the characteristic petroleum hydrocarbon pattern will be altered. When present, these non-petroleum organic compounds will be quantified as part of the TPH; therefore, the analyst must flag the data as presumptively containing significant amounts of non-petroleum compounds.

4.2 Sample contamination due to sample preparation may be minimized by the use of disposable glassware. A prep and a reagent blank are analyzed with each set of 20 or less samples to demonstrate that the system is free from contamination.

4.3 High purity reagent grade or pesticide grade n-pentane and methanol are used to

minimize contamination problems.

4.4 This method depends on correctly integrating a mass of unresolved peaks using a forced baseline. The resulting baseline, if drawn incorrectly, will have a significant effect on the concentration reported. It is imperative that chromatograms be checked (using a realistic scale relative to the chromatogram) for correct baseline extension. Blanks and/or a low level standard should be run to monitor for baseline drift every 10 samples.

5 Health and Safety Issues

The toxicity of the reagents used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) is available to all personnel involved in the chemical analysis.

6 Apparatus

6.1 Glassware

6.1.1 4 oz. (120 milliliters) amber glass wide-mouth jars

6.1.2 10 milliliters glass vials with Teflon-lined screw caps.

6.1.3 40 milliliters glass VOA vials with Teflon lined silicone septa and screw cap.

6.1.4 Disposable pasteur pipets.

6.1.5 10 and 50 milliliters volumetric flasks, Class A.

6.1.6 5, 10 milliliters disposable serological pipets.

6.1.7 5 milliliters glass, gas tight syringe. **All syringes used must be glass, gas-tight syringes.**

6.1.8 18 gauge disposable hypodermic needles. **All needles used during the preparation of the sample(s) should have bore sizes smaller than or equal to an 18 gauge needle.**

6.1.9 Fine glass wool.

6.1.10 2 milliliters autosampler vials with crimp caps having Teflon lined septa.

6.2 Microsyringes: 10 microliter to 1000 microliter

6.3 Analytical balance capable of accurately weighing 0.0001 grams is used for preparation of standards. A top-loading balance capable of weighing to the nearest 0.01 grams should be used for obtaining sample weights.

6.4 Horizontal shakers for soil extraction.

6.5 Drying Oven

6.6 Gas Chromatography

6.6.1 Gas Chromatograph (Shimadzu 17A, Hewlett Packard): Analytical system which includes a split/splitless injector, Electronic Pressure Control (EPC), column, gases, and syringes. A data system (EZChrom), capable of storing and reintegrating chromatographic data and determining peak areas using a forced baseline, baseline projection, and performing baseline compensation is used.

6.6.2 Columns: RTX 5 or RTX-1, 30 m x 0.25 mm x 0.25 µm film thickness. Low bleed columns are preferred. If other columns are used, report the change in the maintenance log book.

6.6.3 Detector: A flame ionization detector (FID) is required.

6.6.4 Autosampler: An autosampler capable of making 1-4 microliter sample injections.

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7 Reagents and Standards

The user of the method should read all relevant Material Safety Data Sheets (MSDSs).

7.1 n-Pentane: Reagent grade, pesticide grade or equivalent, <1milligram residue.

7.2 Acetone (or a water-soluble solvent), pesticide grade or equivalent.

7.3 Methanol: Reagent grade, Purge-and-Trap grade or equivalent, <1 milligram residue.

7.4 Organic Free Reagent Water, ASTM Type II or equivalent.

7.5 Anhydrous Sodium Sulfate, Reagent grade, muffled at 400°C for 4 hours.

7.6 **Calibration & Stock Standard Solutions**: The selected hydrocarbon standard is required for the definition of carbon # retention windows. Standards are prepared in n-pentane as listed in Section 7.1 above.

7.6.1 **Petroleum Product Calibration Standard for Total Petroleum Hydrocarbons:** Petroleum hydrocarbon calibration standards can be purchased from commercial sources. Commercial standard (i.e., Restek) is purchased as a mixture at 50,000 ppm each of gasoline and diesel. Dilute this standard by 10x, by diluting 1 mL of the standard into a final volume of 10 mL of pentane for a concentration of 5000 ug/mL. This is used to prepare the calibration. This standard should be kept refrigerated at -12°C. It is valid for one month. Typical working concentration ranges are 25 to 5000 µg/mL of each product.

7.6.2 **Locator Mix:** This standard is used for retention time window/approximate boiling point distribution marker. The stock standard can be prepared by accurately weighing approximately 0.05 grams of each of n-alkanes of interest, but must include n-hexane (C_6), n-dodecane (C_{12}) and n-octacosane (C_{28}), n-pentatriacontane (C_{35}), surrogate and diluting to volume with 200 mL of n-pentane in a volumetric flask, or by purchasing Window Defining Hydrocarbon Mixed Standard from commercial suppliers. The approximate concentration of this standard solution should be 250 µg/mL per component. This solution is to be used as a marker for retention time window; therefore, accurate concentrations are not necessary. Commercially prepared standards are acceptable.

7.6.3 **Surrogate Stock Solution-** The analyst monitors both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and water blank with surrogate compound that encompass the range of the temperature program used in this method. The surrogate used is o-terphenyl. Prepare by diluting 0.05 grams into 200 mL of 1:1 pentane: acetone for a 250 ppm standard.

7.6.4 **Spike** (2nd source from the calibration standard): Prepare by weighing 1 gram of each gasoline and diesel and diluting to 200 mL with 1:1 pentane: acetone for a 5000 ppm standard. A commercial, second-source standard is acceptable. A commercial, certified standard is acceptable.

8 Sample Collection, Preservation, Containers, and Holding Times

8.1 Solid Samples

8.1.1 If the solid samples are suspected to contain hydrocarbons in the range of C_6 to C_{12} boiling point range, refer to SOP 5035 / SA05-108 when collecting solid samples for volatile analysis and implement the following modifications: The size of the sample for TX1005 analysis that is collected should be approximately 10 g and the sample should be collected using a coring device, extruded into a tared 40 mL VOA vial with a PTFE-lined septum camp, and hermetically sealed in the field.

8.1.2 If hydrocarbons within the C_6 to C_{12} boiling point/carbon range are not suspected, then solid samples may be collected in wide-mouth glass jars with Teflon lined caps.

8.1.3 The holding time for solid samples is 14 days from collection to extraction and 14 days from extraction to analysis. **Prior to extraction, the sample should be held at or below -12 ± 2°C until extraction.** Once extracted, the extract should be tightly capped and **stored at or below -12 ± 2°C** until the time of analysis.

8.2 Aqueous samples

8.2.1 Aqueous samples are to be collected by filling a 40 milliliter VOA vial with Teflon septum without headspace.

8.2.2 Aqueous samples should be preserved with sodium bisulfate, hydrochloric acid or sulfur acid to a pH < 2. The type of preservative and resultant pH should be documented on the field chain of custody documentation.

8.2.3 If the aqueous sample is preserved to a pH of less than 2, the holding time is 14 days from collection to extraction and 14 days from extraction to analysis. If the aqueous sample is not preserved, the holding time is 7 days from collection to extraction and 14 days from extraction to analysis. Prior to extraction, the sample should be held at 4 ± 2°C. Once extracted, the extract should be tightly capped and **stored at or below -12 ± 2°C** until the time of analysis.

9 Procedures

9.1 **Sample Extraction:** Prior to analysis, all samples are extracted with n-pentane. Pressure differences that may develop in a vial during the preparation procedures can be equilibrated using a second needle pierced through the septum while the sample is being taken from the vial using a glass, gas-tight syringe. When n-pentane is being added to the vial and before using a second needle to equilibrate the pressure, enough n-pentane should be added to the vial and mixed in such a way as to capture into the n-pentane any hydrocarbons that may have volatilized into the headspace.

9.1.1 **Soil Extraction.** Extract soil samples using the shaker technique.

9.1.1.1 For samples collected in VOA vials, remove the sample vial from the freezer and allow it to reach room temperature. Dry the outside of the vial. Weigh each vial and its contents on a top loading balance and record the weight to the **nearest 0.01 g**. Subtract the tare weight of the top VOA vial (found on the vial). Record the resulting sample weight. If visible moisture is present, open and quickly add about 5 g sodium sulfate.

9.1.1.2 For samples collected in conventional glass jars, remove the sample container from the freezer and allow it to reach room temperature. Weigh 10 ± 0.01 grams of sample in a 40-mL vial with Teflon cap. Record the weight to the nearest 0.01 grams. If visible moisture is present, open and quickly add about 5 g sodium sulfate.

9.1.1.3 Prepare quality control samples

9.1.1.3.1 Method blank and laboratory control sample (LCS) and laboratory control sample duplicate (LCSD): Prepare by weighing 10 g ± 0.01 g of Ottawa sand or other blank standard solid, into a VOA vial with a PTFE-lined septum cap.

9.1.1.3.2 Matrix Spike/Matrix Spike Duplicate (MS/MSD): For solid MS/MSD, use an appropriate environmental sample, i.e., use the replicate field samples that were collected using the technique in Section 8.1.1, weigh 10 g ± 0.01 g of the environmental bulk sample into a 40-mL vial with a PTFE-lined septum cap.

9.1.1.1.3 Transfer 1.0 mL of Petroleum Spike standard (Section 7.5.4) into the LCS, LCSD, MS, MSD samples using a gas-tight glass syringe. Mix by

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hand shaking for at least 1 minute. The Spike and LCS standard must be from a different source than the calibration standard.

9.1.1.5 Transfer 1.0 mL of the Surrogate Stock Standard (Section 7.5.3) into all samples, including environmental samples, LCS, LCSD, MS, and MSD samples using a gas-tight glass syringe. Mix by hand shaking for at least 1 minute.

9.1.1.6 Add 10 milliliters of n-pentane (9.5 mL pentane + 1.0 mL surrogate or 8.5 mL of pentane + 1.0 mL of surrogate + 1.0 mL of spike) to all samples through the septa of the vial using a 10-mL gas-tight glass syringe and shake by hand at least 1 minute. Let particulate material settle a minimum of 1 hour but can take as long as overnight.

Note: Solids heavily laden with hydrocarbons must be extracted 3 times with 10 mL of n-pentane, transferring the extract each time to a 50-mL graduated cylinder with a ground glass stopper. Measure and record the extract volume on the extraction worksheet.

Note: If particulate is suspended in the solvent layer or an emulsion forms, centrifuge the extract to obtain a clear solvent layer.

9.1.1.7 Uncap the VOA vial and transfer 9-10 mL of the sample extract to a 15 mL vial using a Pasteur pipet. Cap the 15 mL vial with a PTFE-lined cap.

Note: If the extract is to be stored, store the tightly capped vial **at or below -12°C**.

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9.1.2 **Aqueous Extraction.**

9.1.2.1 Remove sample vial from refrigeration and allow to come to ambient temperature. Remove 7 to 8 mL from the vial through the septum seal with a syringe. It is recommended that an additional needle be inserted into the septum to allow for the equalization of pressure as the volume is withdrawn from the vial. Discard. Adjust sample volume by comparison to the reference VOAs. **Two reference 40-mL VOA vials are filled with 35 mL reagent water measured in a class A graduated cylinder. Enough sample is removed from each sample until it is equal to the two VOAs with 35 mL reagent water.**

9.1.2.2 For laboratory method blanks, use a VOA vial filled with 35 mL of reagent water.

9.1.2.3 For matrix spikes and laboratory control samples (LCS), perform the procedure as in Section 9.1.2.1, to a sample or distilled water prior to extraction.

9.1.2.4 Inject 0.4 mL of Petroleum Spike Standard (Section 7.5.4) through the septum into the LCS, LCSD, MS and MSD. Mix by hand shaking for at least 1 minute.

9.1.2.5 Inject 1.0 mL of Surrogate Stock Standard (Section 7.5.3) through the septum into all samples, including environmental samples, LCS, LCSD, MS and MSD samples using a gas-tight glass syringe. Mix by hand shaking for at least 1 minute.

9.1.2.6 Into all samples, inject 2.5 mL of n-pentane (2.0 mL pentane + 1.0 mL surrogate or 1.6 mL pentane + 1.0 mL surrogate + 0.4 mL spike standard) through the septum using a 5-mL syringe.

9.1.2.7 Extract by vigorously shaking for at least 2 minutes.

9.1.2.8 Uncap the vial and fill a 2-mL autosampler vial, using a Pasteur pipet. Cap the autosampler vial with a PTFE-lined cap. A small amount of sodium sulfate is

added to the vial to insure that water was not inadvertently transferred with the pentane.

Note: If the extract is to be stored, store the tightly capped vial **at or below -12°C.**

9.1.3 **Petroleum Samples:** If a sample of neat petroleum product, crude oil, or waste is to be analyzed, the sample should be diluted with n-pentane (1:500 to 1:1000) and analyzed directly.

9.2 **Gas Chromatography**

9.2.1 **Gas Chromatographic Conditions:** These conditions are recommended as a starting point; adjustments may be made to optimize the analysis. Note all changes in the maintenance log book.

9.2.1.1 Oven Program: Set initial column oven temperature to 30°C and hold for 3 minutes. Ramp at 30°C/minute to 325°C, hold for 2.2 minutes (RTX-1) or hold for 7.2 minutes (RTX-5).

9.2.1.2 Sample/autosampler injection: 2.0-µL splitless injection. Split ratio of 3 to 1, 15 seconds after injection.

9.2.1.3 Carrier gas: Helium, 14 mL/min.

9.2.1.4 Make-up gas: Helium

9.2.1.5 FID Hydrogen approximately 30 mL/min and air approximately 300 mL/minute.

9.2.1.6 FID Temperature: 325°C.

9.2.1.7 Injector temperature: 280°C.

9.2.2. Performance Criteria: GC run conditions and columns should be chosen to produce chromatograms with adequate separation of C_6 from C_5 (capable of being integrated as a separate peak). Resolution should be ≥ 50%.

9.2.3 **Retention Time Windows**

9.2.3.1 Retention time windows are established during the method setup and checked every run by analyzing the appropriate mix of marker standards after the method blank analysis. An evaluation is performed to ensure that the response factor for the **C_{35} peak is greater than or equal to 75% of the response factor of the C_{28} peak.** If the response factor for C_{35} is less than 75 % of the response factor for C_{28}, the problem must be corrected and the retention time window re-established for each boiling range. **Be sure to record this evaluation on the chromatogram.**

9.2.3.2 For a given range (e.g., >C_{12} to C_{28}), the retention time (RT) window is defined as beginning 0.1 minutes after the RT of the first marker (e.g., C_{12}) and ending 0.1 minute after the RT of the ending marker compound (e.g., C_{28}). If performed properly for the example range, i.e. >C_{12} to C_{28}, the C_{12} is not included in the reported result and the C_{28} is included in the reported result.

9.2.3.3 Analyst experience is part of the interpretation of the chromatograms and the determination of retention time windows. A default window of ± 0.1 minute is acceptable for this method because of the capillary columns have sufficient overall long term stability to maintain retention time properly. The retention time window should be reassessed for each standard on each GC column during every analytical batch and whenever a new GC column is installed.

9.3 **Calibration:** Calibrate the GC system using the external standard procedure.

9.3.1 **Initial Calibration:** The EZChrom data system is used for data acquisition and processing. The baseline may rise as a result of column bleed at the higher temperatures towards the end of the run. Baseline compensation may help in

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integration of the chromatogram over the background from column bleed.

9.3.1.1 Prepare calibration standards from the stock solution described in Section 7.5.1 at a minimum of five concentration levels. Prepare the following calibration standards from a 5000 ppm stock standard:

Amount of 5000 ppm stock (µL)	Final Volume (mL)	Concentration (µg/mL) *of Each Product*
5	1.0	25
10	1.0	50
20	1.0	100
50	1.0	250
100	1.0	500
200	1.0	1000
500	1.0	2500
1000	1.0	5000

Surrogate Calibration

Amount of Surrogate Std (µL) (7.5.3)	Final Volume (mL)	Concentration (µg/mL)
5	1.0	1.25
10	1.0	2.5
20	1.0	5.0
50	1.0	12.5
100	1.0	25
200	1.0	50
500	1.0	125
1000	1.0	250

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9.3.1.2 Inject each calibration standard using the same injection volume and technique that will be used to introduce the actual samples into the gas chromatograph.

9.3.1.3 Tabulate peak area responses against the concentration injected using a **valley to valley projection**, for approximately C_6 -C_{12} and a **forced baseline** projection for approximately >C_{12} to C_{28}, and >C_{28} to C_{35}. The results are used to prepare a calibration curve for quantitation.

9.3.1.4 The ratio of the response to the amount injected, defined as the response factor (RF), can be calculated for the standard at each concentration. If the percent relative standard deviation (%RSD) is less than or equal to **25%** over the working range. If the %RSD is greater than 25%, then linear regression is used. When linear regression is used for quantitation, the correlation coefficient (r) must be at least 0.995 or $r^2 \geq 0.99$. See the QA Manual calibration section for the applicable equations and guidance.

9.3.1.5 Run an Initial Calibration Verification (ICV) sample immediately after the calibration. The ICV is a mid-level standard made from a source different from the calibration standard. Recovery must be within ±25% of the true value or re-calibrate.

9.3.2 **Calibration Verification:** Before analysis can begin, the working calibration curve is

verified using the following procedures:

9.3.2.1 Analyze a mid-point calibration standard (CCV, same source as calibration curve standard) at the beginning of each working day on which TPH analysis will occur and at the end of each batch of 20 samples, each shift, or each working day, whichever is more frequent.

9.3.2.2 Calculate the relative percent difference. Recalibrate the instrument if the relative percent difference is **> ± 25%**. Reanalyze all sample analyzed after the last acceptable check standard.

9.4 **Gas Chromatographic Analysis**

9.4.1 For samples that contain unresolved hydrocarbons, **baseline projection** should be used to generate the area for TPH calculation or for a group within a defined carbon number. No chromatographic areas related to unresolved hydrocarbons may be disregarded in determining TPH concentration. The GC conditions used for this method produce minimal column bleed up to C_{35}.

9.4.2 If the product concentration exceeds the upper calibration standard in the final extract, the extract should be diluted and reanalyzed.

9.4.3 **Recommended Analytical Batch Sequence:**

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1	Reagent Blank	< MDL
2	Locator	Confirm RT, confirm (area C_{35})/(area C_{28}) > 75%
3	ICV, immediately after calibration	500 mg/L, 75-125% recovery
4	CCV	75-125% recovery
5	Prep Blank	< ½ RL
6	LCS	2nd source, 500 mg/L, 75-125% recovery
7	Matrix Spike	75-125% recovery
8	Matrix Spike	75-125% recovery, 20% RPD with companion spike
9	Samples 1-6	
10	LCSD	2nd source, 500 mg/L, 75-125% recovery, <20% RPD with companion LCS
11	CCV	75-125% recovery
12	CCB	< MDL
13	Samples 7-16	
14	CCV	75-125% recovery
15	CCB	< MDL
16	Samples 17-20	
17	CCV	75-125% recovery
18	CCB	< MDL

9.5 **Calculations**

9.5.1 **TPH Concentration:** The concentration of total TPH (C_6 to C_{35}), selected hydrocarbon ranges (C_6 - C_{12}, >C_{12} - C_{28}, >C_{28} to C_{35}) in a sample can be calculated from the appropriate area using either response factors or regression analysis.

$$C_s = \frac{(C_c)(V_t)(D)}{W_s}$$

where
C_s =Concentration of TPH, hydrocarbon range (mg/L or mg/kg)
C_c =Concentration from calibration curve in micrograms/milliliter (If RF is used for calculations, this value is area response RF)
V_t =Volume of final extract (mL) (The final volume includes the pentane but not the methanol.)
D =Dilution factor
W_s =Weight (grams) or Volume (mL) of sample extracted

9.5.2 **Calibration Factor**

$CF = A/C$

where
CF = Calibration Factor
A = Total area of calibration standard
C = Concentration of calibration standard mg/L

9.5.3 **Percent Relative Standard Deviation**

$\%RSD = (S/x)x100$

where
%RSD = Percent Relative Standard Deviation
S = Standard deviation of the 5 calibration factors.
x = Mean of a minimum of 5 calibration factors.

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9.5.4 **Percent Difference**

$\%D = (CF_x - CF_v) / CF_x \times 100$

where,
%D = Percent difference
CF_x = Average calibration factor
CF_v = Calibration factor of verification standard

9.5.5 **Percent Recovery (LCS and MS/MSD)**

$\%R_{LCS} = (X_m / X_t) \times 100$

where
$\%R_{LCS}$ = Percent recovery LCS
X_m = Measured value
X_t = True Value

$\%R_M = [(SSR-SR) / SA] \times 100$

where
$\%R_M$ = Percent Recovery MS/MSD
SSR = Spiked sample result.
SR = Sample results
SA = Spike added.

9.5.6 **Relative Percent Difference**

$RPD = [(X_1 - X_2) / ((X_1 + X_2) / 2)] \times 100$

where
RPD = Relative percent difference
X_1 = First measured value.
X_2 = Second measured value.

9.5.7 See the QA Manual calibration and QC sections for additional information.

10 Quality Control

10.1 The laboratory maintains a formal and documented quality control program consistent with the NELAC standards and maintains records to document the quality of data generated.

10.2 The quality control procedures necessary to evaluate the GC system operation are found in the QA Manual QC section. Check the performance of the entire analytical system daily using data gathered from analyses of blanks, standards, and replicate samples. If any of the chromatographic QC limits are not met, the analyst should examine the GC system to determine the cause. If the cause of the problem requires shutting down of the GC system, a calibration verification standard should be re-analyzed before any samples are analyzed.

10.2.1 **Method Detection Limits (MDLs):** Prior to analyzing samples, the laboratory determines the method detection limit (MDL) for each instrument used. The guidelines specified in SW-846, 40 CFR Part 136, the QA Manual and SOP MDL / SA08-202 are used to determine the MDL. In general, the MDL should be reported no lower than a value 3 to 5 times below the concentration of the lowest non-zero standard. See the Control Limits Manual for laboratory MDLs.

10.2.2 **Initial Demonstration of Capability.** Each laboratory performing TPH analysis demonstrates the capability to perform assigned components of TPH analysis and meet the acceptance criteria stated below. See the QA Manual and SOP Training / SA08-199 for more details on this demonstration.

10.2.3 For a solid matrix, extract and analyze a minimum of 4 Ottawa sand blanks (10 grams each) spiked with 1 mL of the TPH spike standard (7.5.4) containing the mid-calibration concentration.

10.2.4 For aqueous matrix, extract and analyze a minimum of 4 reagent aqueous blanks spiked with 0.4 of a TPH spike standard (7.5.4) containing the mid-point calibration concentration.

10.2.5 Calculate the following:
- TPH of each sample for carbon range C_6 to C_{35}.
- Average percent recovery; and
- Relative standard deviation

10.2.6 **Average Percent recovery should be between 75% and 125%. Relative standard deviation should be ± 20%.**

10.2.7 Repeat the initial demonstration of capability if:
- A change is made in instrument type, personnel, or matrix;
- A laboratory or analyst is unable to meet acceptance criteria for the demonstration of capability:
- A new analyst(s) is trained on this method; or
- Quality systems, method-related, or operational problems having the potential to affect data quality are suspected or confirmed.

10.3 **Performance Evaluation Sample**

Successfully analyze available performance evaluation samples from an independent

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commerical source for both solid and aqueous samples at both low (5-10 mg/L for aqueous and 50-100 mg/kg for solid) and high (20-100 mg/L for aqueous and 1000-20000 mg/kg for solid) concentrations. Data and chromatograms for these samples are kept on file at the laboratory. The laboratory analyzes performance evaluation samples annually.

10.4 **Instrument Quality Control**

10.4.1 The n-hexane (C_6) peak must be adequately resolved (capable or being integrated as an independent peak) from the n-pentane (C_5) solvent in the chromatographic run. Resolution should be > 50%.

10.4.2 Retention time windows are established for n-hexane (C_6), n-dodecane (C_{12}), n-octacosane (C_{28}) and n-pentatricontane (C_{35}), or for each carbon marker in the alternated carbon locator mix, each time a new GC column is installed and is verified and/or adjusted on a daily basis, i.e., *once per sequence*.

10.4.3 Calibration curves are developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 25%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) must be least 0.995 (or $r^2 \geq 0.99$). Each laboratory must generate control limits based on the average recovery ± 3 standard deviations as determined from the results of the laboratory control sample. These control limits must be within 75% to 125% recovery and should be statistically generated and used to control the analytical system.

10.4.4 A summary of quality control checks, the minimum frequency at which those checks should be performed, the acceptance criteria those checks should meet, and the corrective action(s) that should be taken if the acceptance criteria are not met are presented in Table 8-1. All data associated with quality control checks not meeting the acceptance criteria should be flagged by the laboratory to advise the data user.

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Table 8-1
Summary of Calibration and QC Procedures for TNRCC Method 1005

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Minimum 5-point initial calibration	Initial calibration prior to sample analysis	Mean RSD for TPH < 25% or correlation coefficient r for linear regression ≥ 0.995 (or $r^2 \geq 0.99$).	Correct the problem then repeat initial calibration
Initial Calibration Verification (ICV) – Second Source Standard	Immediately after calibration	75-125% recovery	Correct the problem, then repeat ICV.
Calibration Verification – Same source as calibration	At the beginning of each working day on which TPH analysis will occur and at the end of each batch of 20 samples, each shift, or each working day, whichever is more frequent.	RPD < ± 25% of expected value.	Correct problem then repeat initial calibration.

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Demonstrate ability to generate acceptable accuracy and precision using 4 replicate analyses of a QC check sample.	Initially prior to analysis of any samples and in response to changes in staff, instrumentation, or operations.	Average %R within 75%-125% and RSD < ± 20% or within laboratory limits.	Recalculate results; locate and correct problem with system and then rerun demonstration for those analytes that did not meet criteria.
Method blank	One per analytical batch of 20 samples or less.	No TPH detected > MDL.	Correct problem, then re-prep and analyze method blank and all samples processed with the contaminated blank.
LCS and LCSD	One LCS/LCSD per analytical batch of 20 samples or less.	%R within 75-125% and RPD < ± 20% or within laboratory limits.	Correct problem then re-prep and analyze LCS and all samples in the affected analytical batch.
MS/MSD	One MS/MSD per every 20 project samples per matrix.	%R within 75-125% and RPD < ± 20% or within laboratory limits.	None.
Retention time window and discrimination check	Once, at the start of the analytical batch of 20 samples or less.	The area for C_{35} ≥ 75% of the area for C_{28}*.	Correct problem then reestablish the RT windows and re-analyze all samples analyzed since the last retention time checked.
Surrogate Recoveries	Spiked into every sample including all QC samples	%R within 70-130% or laboratory established limits	Reanalyze, or re-extract and reanalyze, or flag the data (whichever is most appropriate)
Performance Evaluation Samples	Once per 12 month period	Within manufacturer's statistical guidelines.	Re-extract/reanalyzed. If still out, correct the problem and reanalyze.
MDL study	Once per 12 month period	Detection limits established shall be < ½ the RLs	None.
All corrective actions associated with project work should be documented, and all records should be maintained by the laboratory. *RF is not applicable as it is not used for quantitation; only as RT check.			

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11 Data Reduction and Reporting

The following information and data should be reported: The calculated concentrations of TPH, as dry weight: C_6 to C_{12} , >C_{12} to C_{28}, >C_{28} to C_{35} and Total C_6 to C_{35} = ((C_6 to C_{12}) +(>C_{12} to C_{28}) + (>C_{28} to C_{35})).

12 Method Performance

12.1 If there is an indication that a significant portion of material may be present in a sample above C_{35} (indicated by a raised baseline that does not readily return to the initial

baseline), it is possible that this sample may contain petroleum hydrocarbons that are too heavy to be adequately characterized by GC analysis. This sample should also be analyzed by EPA Method 1664 (with silica clean up) to determine the concentration of the heavy material gravimetrically.

12.2 The laboratory method performance may be shown with the use of control charts. See the QA department for this information.

13 Pollution Prevention

13.1 The solvent used in this method poses little threat to the environment when recycled and managed properly.

13.2 The quantity of chemicals purchased should be based on the expected usage during its shelf life. Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

13.3 It is TestAmerica Analytical Testing Corp.'s policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

14 Waste Management

14.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly to comply the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

14.2 Laboratory waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the QA Manual and SOP Waste Disposal / SA10-83.

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15 References

15.1 QA Manual

15.2 Control Limits Manual

15.3 SOPs: Waste Disposal / SA10-83, Training / SA08-199 (Training), and SA08-202 (MDLs).

ADDITIONAL SECTIONS:

16 Contingencies

If for any reason a part of this SOP cannot be followed, seek the guidance of the Department Supervisor of the Laboratory Technical Director. All abnormalities must be noted on the data or the benchsheet, in the Non-conformance Database, and in Element. See the corrective action section and Appendix 4 of the QA Manual.

17 Attachments

None.

APPENDIX D

FIELD FORMS

Tetra Tech NUS, Inc.

SOIL & SEDIMENT SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____
Project No.: _____

[] Surface Soil
[] Subsurface Soil
[] Sediment
[] Other: _____
[] QA Sample Type: _____

Sample ID No.: _____
Sample Location: _____
Sampled By: _____
C.O.C. No.: _____

Type of Sample:
[] Low Concentration
[] High Concentration

GRAB SAMPLE DATA:

Date:	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Time:			
Method:			
Monitor Reading (ppm):			

COMPOSITE SAMPLE DATA:

Date:	Time	Depth Interval	Color	Description (Sand, Silt, Clay, Moisture, etc.)
Method:				
Monitor Readings (Range in ppm):				

SAMPLE COLLECTION INFORMATION:

Analysis	Container Requirements	Collected	Other

OBSERVATIONS / NOTES:

MAP:

Circle if Applicable:

MS/MSD	Duplicate ID No.:

Signature(s):

Tetra Tech NUS, Inc.

EQUIPMENT CALIBRATION LOG

PROJECT NAME : _____ INSTRUMENT NAME/MODEL: _____

SITE NAME: _____ MANUFACTURER: _____

PROJECT No.: _____ SERIAL NUMBER: _____

Date of Calibration	Instrument I.D. Number	Person Performing Calibration	Instrument Settings		Instrument Readings		Calibration Standard (Lot No.)	Remarks and Comments
			Pre-calibration	Post-calibration	Pre-calibration	Post-calibration		

Tetra Tech NUS, Inc.

BORING LOG

Page ___ of ___

PROJECT NAME: _____ BORING No.: _____
PROJECT NUMBER: _____ DATE: _____
DRILLING COMPANY: _____ GEOLOGIST: _____
DRILLING RIG: _____ DRILLER: _____

Sample No. and Type or RQD	Depth (Ft.) or Run No.	Blows / 6" or RQD (%)	Sample Recovery / Sample Length	Lithology Change (Depth/Ft.) or Screened Interval	MATERIAL DESCRIPTION: Soil Density/ Consistency or Rock Hardness	Color	Material Classification	USCS *	Remarks	PID/FID Reading (ppm): Sample	Sampler BZ	Borehole**	Driller BZ**

* When rock coring, enter rock brokeness.

** Include monitor reading in 6 foot intervals @ borehole. Increase reading frequency if elevated reponse read.

Drilling Area Background (ppm): [ ]

Remarks: _____

Converted to Well: Yes _____ No _____ Well I.D. #: _____

TETRA TECH NUS, INC. CHAIN OF CUSTODY | NUMBER 0584 | PAGE ____ OF _____

PROJECT NO:	FACILITY:	PROJECT MANAGER	PHONE NUMBER	LABORATORY NAME AND CONTACT:
SAMPLERS (SIGNATURE)		FIELD OPERATIONS LEADER	PHONE NUMBER	ADDRESS
		CARRIER/WAYBILL NUMBER		CITY, STATE

STANDARD TAT ☐
RUSH TAT ☐
☐ 24 hr. ☐ 48 hr. ☐ 72 hr. ☐ 7 day ☐ 14 day

CONTAINER TYPE PLASTIC (P) or GLASS (G)

PRESERVATIVE USED

TYPE OF ANALYSIS

DATE YEAR	TIME	SAMPLE ID	LOCATION ID	TOP DEPTH (FT)	BOTTOM DEPTH (FT)	MATRIX (GW, SO, SW, SD, QC, ETC.)	COLLECTION METHOD GRAB (G) COMP (C)	No. OF CONTAINERS									COMMENTS

1. RELINQUISHED BY	DATE	TIME	1. RECEIVED BY	DATE	TIME
2. RELINQUISHED BY	DATE	TIME	2. RECEIVED BY	DATE	TIME
3. RELINQUISHED BY	DATE	TIME	3. RECEIVED BY	DATE	TIME

COMMENTS

DISTRIB : WHITE (ACCOMPANIES SAMPLE) YELLOW (FIELD COPY) PINK (FILE COPY)

4/02R

FORM NO. TINUS 001

Tetra Tech NUS, Inc.

FIELD PORTABLE XRF SAMPLE ANALYSIS LOG SHEET

Project Site Name: _____ Measurement Units: _____

Project No: _____ Run Length/Duration _____

Analyzer: _____ Analysis Date: _____

Sample ID	Analysis Time	Element Analysis	Result Run 1	Result Run 2	Result Run 3	Results Avg.	Comments

Notes:

Tetra Tech NUS, Inc.

QA SAMPLE LOG SHEET

Page___ of ___

Project Site Name: _____ Sample ID Number: _____
Project Number: _____ Sampled By: _____
Sample Location: _____ C.O.C. Number: _____
QA Sample Type:

[] Trip Blank [] Rinsate Blank
[] Source Water Blank [] Other Blank _____

SAMPLING DATA:

Date: _____
Time: _____
Method: _____

WATER SOURCE:

[] Laboratory Prepared [] Tap
[] Purchased [] Fire Hydrant
[] Other _____

PURCHASED WATER INFORMATION (If Applicable as Source or Rinsate Water):

Product Name: _____
Supplier: _____
Manufacturer: _____
Order Number: _____
Lot Number: _____
Expiration Date: _____

RINSATE INFORMATION (If Applicable):

Media Type: _____
Equipment Used: _____
Equipment Type:

[] Dedicated
[] Reusable

SAMPLE COLLECTION INFORMATION:

Analysis	Preservative	Container Requirements	Collected
Volatiles	Cool 4°C & HCl		YES / NO
Semivolatiles	Cool 4°C		YES / NO
Pesticide / PCB	Cool 4°C		YES / NO
Metals	Cool 4°C & HNO_3		YES / NO
Cyanide	Cool 4°C & NaOH		YES / NO

OBSERVATIONS / NOTES:

Signature(s):

EQUIPMENT INSPECTION

COMPANY:_____ UNIT NO._____

FREQUENCY: Inspect at the initiation of the project, after repairs, once every 10-day shift.

Inspection Date: ____/____/____ Time: _____ Equipment Type:_____
(e.g., bulldozer, generator)

	Good	Need Repair	N/A
Tires or tracks	☐	☐	☐
Hoses and belts	☐	☐	☐
Cab, mirrors, safety glass	☐	☐	☐
- Turn signals, lights, brake lights, etc. (front/rear) for equipment approved for highway use?	☐	☐	☐
- Is the equipment equipped with audible back-up alarms and back-up lights?	☐	☐	☐
Horn and gauges	☐	☐	☐
Brake condition (dynamic, park, etc.)	☐	☐	☐
Fire extinguisher (Type/Rating -_____)	☐	☐	☐
Fluid Levels:			
- Engine oil	☐	☐	☐
- Transmission fluid	☐	☐	☐
- Brake fluid	☐	☐	☐
- Cooling system fluid	☐	☐	☐
- Windshield wipers	☐	☐	☐
Hydraulic oil	☐	☐	☐
Oil leak/lube	☐	☐	☐
Coupling devices and connectors	☐	☐	☐
Exhaust system	☐	☐	☐
Blade/boom/ripper condition	☐	☐	☐
Access-ways: Frame, hand holds, ladders, walkways (non-slip surfaces), guardrails?	☐	☐	☐
Power cable and/or hoist cable	☐	☐	☐
Steering (standard and emergency)	☐	☐	☐

Safety Guards:

	Yes	No
– Around rotating apparatus (belts, pulleys, sprockets, spindles, drums, flywheels, chains) all points of operations protected from accidental contact?_____	☐	☐
– Hot pipes and surfaces exposed to accidental contact?_____	☐	☐
– All emergency shut offs have been identified and communicated to the field crew?_____	☐	☐
– Have emergency shutoffs been field tested? _____	☐	☐
– Results?_____	☐	☐
Are any structural members bent, rusted, or otherwise show signs of damage?_____	☐	☐
– Are fueling cans used with this equipment approved type safety cans?_____	☐	☐

EQUIPMENT INSPECTION (Continued)

- Have the attachments designed for use (as per manufacturer's recommendation) with this equipment been inspected and are considered suitable for use?_____ ☐ ☐

Portable Power Tools:

- Tools and Equipment in Safe Condition?_____ ☐ ☐
- Saw blades, grinding wheels free from recognizable defects (grinding wheels have been sounded)? ☐ ☐
- Portable electric tools properly grounded?_____ ☐ ☐
- Damage to electrical power cords?_____ ☐ ☐
- Blade guards in place?_____ ☐ ☐
- Components adjusted as per manufacturers recommendation?_____ ☐ ☐

Cleanliness:

- Overall condition (was the decontamination performed prior to arrival on-site considered acceptable)?_____
- Where was this equipment used prior to its arrival on site?_____
- Site Contaminants of concern at the previous site?_____
- Inside debris (coffee cups, soda cans, tools and equipment) blocking free access to foot controls?_____

Operator Qualifications (as applicable for all heavy equipment):

- Does the operator have proper licensing where applicable, (e.g., CDL)?_____
- Does the operator, understand the equipment's operating instructions?_____
- Is the operator experienced with this equipment? _____
- Does the operator have emotional and/or physical limitations which would prevent him/her from performing this task in a safe manner?_____
- Is the operator 21 years of age or more?_____

Identification:

- Is a tagging system available, for positive identification, for tools removed from service?___

Additional Inspection Required Prior to Use On-Site

	Yes	No
Does equipment emit noise levels above 90 decibels?	☐	☐
If so, has an 8-hour noise dosimetry test been performed?	☐	☐

- Results of noise dosimetry:_____
- Defects and repairs needed:_____
- General Safety Condition: _____
- Operator or mechanic signature:_____

Site Safety Officer Signature:_____

Approved for Use: ☐ Yes ☐ No

SITE-SPECIFIC TRAINING DOCUMENTATION

My signature below indicates that I am aware of the potential hazardous nature of performing remedial investigation activities at _____ and that I have received site-specific training which included the elements presented below:

- Names of designated personnel and alternates responsible for site safety and health
- Safety, health, and other hazards present at the sites
- Use of personal protective equipment
- Safe use of engineering controls and equipment
- Medical surveillance requirements
- Signs and symptoms of overexposure
- Contents of the Health and Safety Plan
- Emergency response procedures (evacuation and assembly points)
- Initial response procedures
- Review of the contents of relevant Material Safety Data Sheets
- Review of the use of Safe Work Permits

I have been given the opportunity to ask questions and all of my questions have been answered to my satisfaction. I further state, that the dates of my training (introductory, refresher, and supervisory, as applicable) and my medical surveillance requirements are accurate and correct to the best of my knowledge.

Name (Printed and Signature)	Site-Specific Training Date	40-Hour Training (Date)	8-Hour Refresher Training (Date)	8-Hour Supervisory Training (Date)	Medical Exam

MEDICAL DATA SHEET

This Medical Data Sheet must be completed by all on-site personnel and kept in the command post during the conduct of site operations. This data sheet will accompany any personnel when medical assistance is needed or if transport to hospital facilities is required.

Project _____

Name _____ Home Telephone _____

Address _____

Age _____ Height _____ Weight _____

Name of Next Kin _____

Drug or other Allergies _____

Particular Sensitivities _____

Do You Wear Contacts? _____

Provide a Checklist of Previous Illnesses or Exposure to Hazardous Chemicals _____

_____

_____

What medications are you presently using? _____

_____

_____

Do you have any medical restrictions? _____

_____

_____

Name, Address, and Phone Number of personal physician: _____

_____

_____

I am the individual described above. I have read and understand this HASP.

_____ _____

Signature Date

APPENDIX E

DISCUSSION OF SAMPLING SIZE CALCULATION

DISCUSSION OF SAMPLING SIZE CALCULATION

Taking advantage of the expectation that there will be at each site an area of contaminated soil within an area of uncontaminated soil, a stratified sampling design was proposed. This required each area of significantly different concentration level to be treated as a single population. By doing this, the mean and standard deviation expected for the samples to be collected within each stratum would be different and this difference typically allows a lesser total number of samples to be collected while still meeting the specified decision performance. Do to the uses of the ranges present there are two stratified sampling plans that will be used. In the first situation the range will be split into two strata a clean, and a dirty. In the second situation the range will be split into three strata a clean, a dirty, and a transition stratum. For both situations the following inputs and assumptions were used:

- Null hypothesis (baseline condition) = Remedial action is needed.
- Chance of not taking action when it should be taken (alpha) = 15 percent.
- Chance of taking action when it should not be taken (alpha) = 25 percent.
- The contaminated area would be remediated so it is no more contaminated than the uncontaminated area.
- A typical estimate for standard deviation of data is equal to the range of expected concentrations divided by six. (The conservative approach of taking the maximum value divided by six was used so this would give us a larger standard deviation and thus larger sample size estimates).

By separating the site into two strata, there is a set of performance criteria for each stratum:

<u>Stratum #1 (Clean area):</u>

AL=400
Range of Values: 0-600
Mean = 250;
Alpha = 15 percent;
Beta = 25 percent;
Std. Dev. = 600/6 =100
Delta = difference from mean to AL = 150
Number of samples = 5

Stratum #2 (Contaminated area)

AL = 400
Range of Values = 2,000-50,000
Mean = 15000;
Alpha = 15 percent;
Beta = 25 percent;
Std. Dev. = 50000/6 = 8333
Delta = difference from mean to AL= 14600
Number of samples = 5

For the second situation where there are 3 stratums present

By separating the site into three strata, there is a set of performance criteria for each stratum:

Stratum #1 (Clean area)

AL = 400
Range of Values: 0-600
Mean = 250;
Alpha = 15 percent;
Beta = 25 percent;
Std. Dev. = 600/6 =100
Delta = difference from mean to AL= 150
Number of samples = 5

Stratum #2 (Transition Zone)

AL = 400
Range of Values: 400-5000
Mean = 2000;
Alpha = 15 percent;
Beta = 25 percent;
St. Dev. = 5000/6=833
Delta = difference from mean to AL= 1600
Number of samples = 5

Stratum #3 (Dirty)

AL = 400
Range of Values: 2000-50000;
Mean = 15000;
Alpha = 15 percent;
Beta = 25 percent;
St. Dev. = 50000/6=8333
Delta = difference from mean to AL= 14600
Number of samples = 5