QUALITY ASSURANCE PROJECT PLAN

PORTAGE CREEK AREA REMOVAL KALAMAZOO, MICHIGAN

Prepared for:

U.S. Environmental Protection Agency
Region 5

Prepared by:

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QUALITY ASSURANCE PROJECT PLAN
FOR

PORTAGE CREEK AREA
TIME CRITICAL REMOVAL ACTION
KALAMAZOO, MICHIGAN
NPL STATUS: NPL SITE

Prepared for

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

By

ENVIRONMENTAL QUALITY MANAGEMENT, INC.
U.S. EPA Contract No. EP-S5-08-02
Task Order No. 0087

September 2011 (Revision 0)

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ACRONYMS

°C	degrees Celsius
≥	greater than or equal to
≤	less than or equal to
<	less than
±	plus or minus
%	percent
%D	percent difference
µg	microgram
µm	micrometer
A	
AA	atomic absorption
ALs	action levels
BFB	bromofluorobenzene
Bgs	below ground surface
CAS	chemical abstract service
CCC	calibration check compounds
CLP NFG	Contract Laboratory Program National Functional Guidelines
CN	cyanide
COC	chain of custody
cy	cubic yards
DCB	dichlorobenzenee
DI	deionized
DQI	data quality indicators
DQO	data quality objectives
Dup	duplicate
ECD	electron capture detector
EDD	electronic data deliverable
EHS	Environmental Health and Safety
EQ	Environmental Quality Management
ERRS	Emergency and Rapid Response Services
FD	field duplicate
FSP	Field Sampling Plan
ft	feet
GC	gas chromatograph
Gl	glass
GPS	global positioning system
H_2SO_4	sulfuric acid
HASP	Health and Safety Plan
HAZWOPER	Hazardous Waste Operations and Emergency

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ACRONYMS – CONTINUED

IC	ion chromatography
ICAL	initial calibration
ICP	inductively coupled plasma
ICV	initial calibration verification
ID	identification
in	inch
kg	kilogram
L	liter
LCS	laboratory control sample
LDC	Laboratory Data Consultants
m^3	cubic meter
MDEQ	Michigan Department of Environmental Quality
MDNR	Michigan Department of Natural Resources
MDL	method detection limit
ml	milliliter
mg	milligram
mm	millimeter
MS	mass spectroscopy
MS/MSD	matrix spike/matrix spike duplicate
NA	not applicable
NaOH	sodium hydroxide
NIOSH	National Institute for Occupational Safety and Health
No.	number
NTU	nephelometric turbidity units
OSC	On-Scene Coordinator
OUs	Operational Units
oz	ounce
PCB	polychlorinated biphenyls
PEL	permissible exposure limit
Pl	Plastic
PM	Project Manager
ppm	parts per million
PQO	project quality objectives
PVC	poly vinyl chloride
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
r	correlation coefficient
RBSLs	Rick Based Screening Levels

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ACRONYMS – CONTINUED

RCRA	Resource Conservation and Recovery Act
RF	response factor
RL	reporting limit
RM	Response Manager
RPD	relative percent difference
RRFs	relative response factors
RSD	relative standard deviation
sf	square feet
SM	Standard Methods
SMO	Sample Management Office
SOP	standard operating procedure
SPCC	System performance check compounds
START	Superfund Technical and Response Team
SU	sample unit
Surr.	surrogate
SVOCs	semivolatile organic compounds
SW	surface water
TAL	target analyte list
TBD	to be determined
TCL	target compound list
TCLP	toxicity characteristic leaching procedure,
TCMX	Tetrachloro-m-xylene
TCRA	Time Critical Removal Action
TDD	Technical Direction Document
TSCA	Toxic Substances Control Act
TSS	total suspended solids
UFP	Uniform Federal Policy
U.S. EPA	United States Environmental Protection Agency
V	five
VOCs	volatile organic compounds
WESTON	Weston Solutions
WM	widemouth
WP	Work Plan

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QAPP Worksheet #1 Title and Approval Page

Site Name/Project Name: Portage Creek Area Site
Site Location: Kalamazoo, Kalamazoo County, Michigan

Quality Assurance Project Plan (QAPP) for the Portage Creek Area Site
Document Title

United States Environmental Protection Agency (U.S. EPA) Region V
Lead Organization

Jackie Doan, Environmental Quality Management, Inc. (EQ) Emergency and Rapid Response Services (ERRS) Contractor
Preparer's Name and Organizational Affiliation

1800 Carillon Blvd, Cincinnati, OH 45240, jdoan@eqm.com
Preparer's Address, Telephone Number, and E-mail Address

August 5, 2011
Preparation Date (Day/Month/Year)

Investigative Organization's Project Manager:_____
Signature

Eric Bowman, EQ, ERRS Contractor, September 29, 2011
Printed Name/Organization/Date Printed

Investigative Organization's Project QA Officer:_____
Signature

Jackie Doan, EQM ERRS Contractor, September 29, 2011
Printed Name/Organization/Date

Lead Organization's Project Manager:_____
Signature

Sam Borries, U.S. EPA Region V, September 29, 2011
Printed Name/Organization/Date

Approval Signatures:_____
Signature

_____
Printed Name/Title/Date

Approval Authority_____

Other Approval Signatures:_____
Signature

_____
Printed Name/Title/Date

Document Control Number: 3281-87PCA.1

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QAPP Worksheet #2 QAPP Identifying Information

Site Name/Project Name: Portage Creek Area Site
Site Location: Kalamazoo, Kalamazoo County, Michigan (see Figure 1)
Site Number/Code:
Operable Unit: OU5
Contractor Name: Environmental Quality Management, Inc. (EQ)
Contractor Number: EP-S5-08-02
Contract Title: Emergency and Rapid Response Services (ERRS)
Work Assignment Number: 087

1. Identify guidance used to prepare QAPP:

   Uniform Federal Policy for Quality Assurance Project Plans, March 2005

2. Identify regulatory program: United States Environmental Protection Agency (U.S. EPA) Region V, Emergency Response Branch

3. Identify approval entity: U.S. EPA Region V

4. Indicate whether the QAPP is a generic or a project-specific QAPP. (circle one)

5. List dates of scoping sessions that were held: There have been several scoping meetings associated with this project. EQ held a scoping session on July 15, 2011.

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

Title	Approval Date

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

8. List data users: U.S. EPA Region V, On-Scene Coordinators (OSC) Sam Borries, Paul Ruesch and Craig Tomas

9. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below: _____

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Worksheet #2 – continued

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Worksheet No. or Related Documents
Project Management and Objectives		
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2.2 Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.4 QAPP Identifying Information	- Table of Contents - QAPP Identifying Information	2 2
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2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	- Project Scoping Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History, and Background - Site Maps (historical and present)	9 9 10 10
2.6 Project Quality Objectives and Measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	- Site-Specific PQOs - Measurement Performance Criteria Table	11 12
2.7 Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations Table	13 13
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation Table - Project Schedule/Timeline Table	14 15 16

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Worksheet #2 – continued

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Worksheet No. or Related Documents
Measurement/Data Acquisition		
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	- Sampling Design and Rationale - Sample Location Map - Sampling Locations and Methods/ SOP Requirements Table - Analytical Methods/SOP Requirements Table - Field QC Sample Summary Table - Sampling SOPs - Project Sampling SOP References Table - Field Equipment Calibration, Maintenance, Testing, and Inspection Table	17 17 18 19 20 Appendix A 21 22
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Worksheet #2 – continued

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Worksheet No. or Related Documents
Assessment/Oversight		
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5.3 Streamlining Data Review 5.3.1 Data Review Steps To Be Streamlined 5.3.2 Criteria for Streamlining Data Review 5.3.3 Amounts and Types of Data Appropriate for Streamlining		

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QAPP Worksheet #3 Distribution List

QAPP Recipients	Title	Organization	Telephone Number	E-mail Address	Document Control Number
Sam Borries	OSC	U.S. EPA	312-353-8360	Borries.samuel@epamail.epa.gov	
Chris Lantinga	START Project Manager (PM)	WESTON	616-550-5358	Christopher.Lantinga@westonsolutions.com	
Tonya Balla	START Sample Management Coordinator / Project Quality Assurance (QA) Officer	WESTON	847-918-4094	t.balla@westonsolutions.com	
Mike Browning	START Site Contact	WESTON	248-259-4761	mbrowning@dynamac.com	
Eric Bowman	ERRS Response Manager (RM)	EQ	513-265-8875	ebowman@eqm.com	
Jeff Rhinefield	ERRS Site RM	EQ	513-309-4703	jrhinefield@eqm.com	
Jackie Doan	ERRS Sample Management Coordinator / Project QA Officer	WESTON	513-673-4210	jdoan@eqm.com	
TBD	ERRS Site Sample Manager	EQ			
Taryn M. Mancine	Lab PM	Test America Laboratories, Inc.	937-294-6856	taryn.mancine@testamericainc.com	

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QAPP Worksheet #4 Project Personnel Sign-Off Sheet

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Sam Borries	U.S. EPA OSC	312-802-5336		
Chris Lantinga	START PM	616-550-5358		
Tonya Balla	START Project QA Officer	847-918-4094		
Eric Bowman	ERRS RM	513-265-8875		
Jeff Rhinefield	ERRS Site RM	513-309-4703		
Jackie Doan	ERRS Sample Management Coordinator / Project QA Officer	513-673-4210		
TBD	ERRS Site Sample Coordinator			

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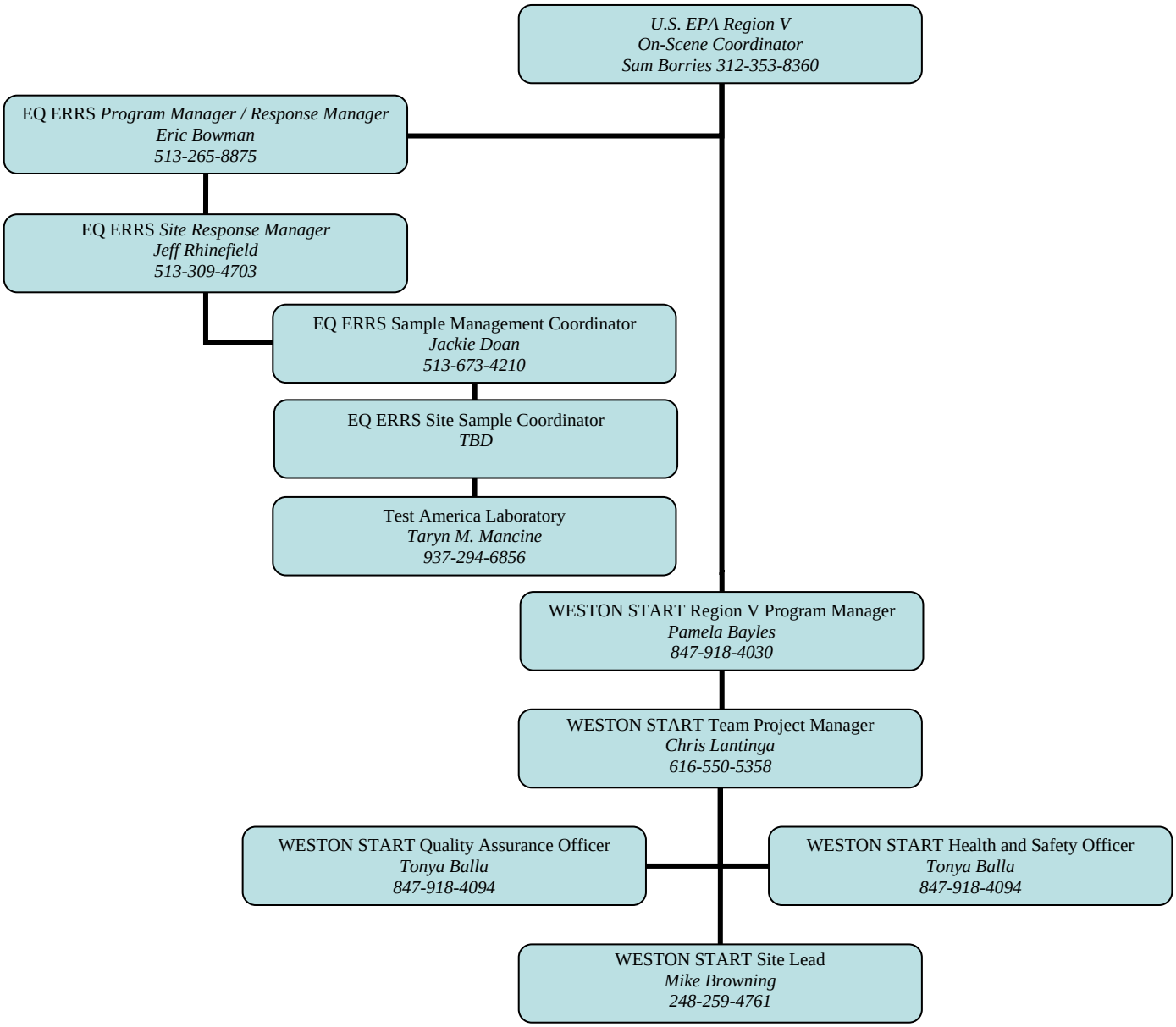
QAPP Worksheet #5 Project Organizational Chart



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QAPP Worksheet #6 Communication Pathways

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Project scope changes	U.S. EPA OSC	Sam Borries	312-353-8360	The OSC will inform the WESTON PM and the ERRS RM of any project scope changes. The WESTON PM and ERRS RM will in turn inform their respective program managers of the changes.
Management of required project tasks for START	START PM	Chris Lantinga	616-550-5358	The WESTON PM will inform the appropriate WESTON project staff (field and non-field) of tasks to complete and the required completion date. The WESTON project staff will communicate with the PM of task progress and resources/information required to complete tasks.
Management of required project tasks for ERRS	ERRS RM	Eric Bowman	513-265-8875	The ERRS RM will inform the appropriate ERRS staff, including subcontractors, (field and non-field) of tasks to complete and the required completion date. The ERRS project staff will communicate with the RM of task progress and resources/information required to complete tasks.
Delays or changes to field work	ERRS RM	Eric Bowman	513-265-8875	The ERRS RM will inform the OSC and WESTON Site Leader of any delays or changes to field work while on site. The WESTON Site Leader will inform the WESTON PM of delays or changes to field work by email or telephone.
Field Activities / Progress	ERRS Site RM	Jeff Rhinefield	513-309-4703	The ERRS Site Response Manager will inform the ERRS Sample Management Coordinator of any field related issues impacting the sample schedule or sample quality.
Daily field updates	ERRS Sample Management Coordinator / Project QA Officer	Jackie Doan	513-673-4210	The ERRS Site Response Manager will inform the ERRS Sample Management Coordinator who will report to the OSC and WESTON Site Leader of daily field progress while on site. The WESTON Site Leader will provide the WESTON Project Manager with any pertinent information contained in the daily updates by telephone or email.

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Worksheet #6 – continued

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Reporting of Laboratory Data Quality Issues	Sample Management Coordinator	Jackie Doan / Tonya Balla	513-673-4210/ 847-918-4094	The Sample Management Coordinator will inform the OSC of any issues related to data quality upon receipt of samples or during analyses. Note that both the ERRS and START contractors will be procuring laboratories for the removal action. Therefore, there are two sample management coordinators for this project – one for ERRS and one for START.
Recommendations to stop work and initiation of corrective actions	OSC/ ERRS RM/START QA Officer	Sam Borries/ Eric Bowman/ Tonya Balla	312-353-8360/ 513-265-8875/ 847-918-4094	The OSC, ERRS RM, and START QA Officer all have the authority to stop work and initiate corrective actions should there be a reason to do so. Whoever stops the work or initiates corrective actions will inform the other interested parties such as the WESTON Site Leader, OSC, or RM. The Site Leader will inform the WESTON PM of stop work orders and corrective actions.
Distribution of analytical data	Sample Management Coordinator	Jackie Doan/ Tonya Balla	513-673-4210 / 312-424-3339	The Sample Management Coordinator will receive all deliverables from the laboratory and distribute them to the OSC. The data will not be distributed further until it has been reviewed and validated by an ERRS or START Chemist. The OSC will distribute the validated data to other interested parties.
Approval of QAPP Amendments	OSC	Sam Borries	312-353-8360	Approval of all QAPP amendments will be by the OSC prior to the changes being implemented.

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QAPP Worksheet #7 Personnel Responsibilities and Qualifications Table

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Sam Borries	OSC	U.S. EPA Region V	The OSC or his designee has overall project authority and directs the WESTON Project Manager and ERRS Response Manager regarding the tasks required to meet project objectives. The OSC is also responsible for reviewing and approving the project-specific QAPP (and any amendments) prior to its implementation.	Federal OSC
Pamela Bayles	START Region V Program Manager	WESTON	The START Program Manager is responsible for ensuring the quality of work performed under the Region V START III contract. The START Program Manager interfaces directly with the U.S. EPA Contracting Officer and Project Officer, and has overall responsibility and direction for task assignments.	M.E.M. (Masters in Environmental Management), Air and Water Resources; B.S., Biology; over 18 years experience
Chris Lantinga	START PM	WESTON START	The project manager is responsible for managing all START aspects of the project, WESTON project personnel, and WESTON subcontractors. The project manager interfaces directly with the U.S. EPA OSC regarding all START project tasks.	B.A. Engineering/Geology, B.S. Civil Engineering, over 17 years of experience
Tonya Balla	START QA Officer	WESTON START	The START QA Officer reviews the project QAPP and has overall responsibility for START project QA. The QA Officer will also perform a compliance check of all data reviewed and validated by the ERRS or START Chemist.	B.S. Environmental Engineering; over 18 years' experience
Tonya Balla	Health and Safety Officer	WESTON START	The health and safety officer approves the Health and Safety Plan and provides guidance to WESTON field personnel on health and safety issues.	B.S. Environmental Engineering; over 18 years experience
Mike Browning	START Site Leader	WESTON START	The site leader manages the field team and all START work performed in the field. The site leader interfaces directly with the WESTON project manager regarding field tasks and any issues that arise while in the field.	M.S. Natural Resources Policy, B.S. Environmental Policy, over 10 years of experience
Eric Bowman	ERRS RM	EQ ERRS	The ERRS Response Manager is responsible for managing the removal action tasks. For the Site removal action to occur this includes subcontracting (if necessary) and managing sediment removal, sediment, and restoration.	B.S. Geology, over 25 years of experience

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Worksheet #7 – continued

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Jeff Rhinefield	ERRS Site RM	EQ ERRS	The ERRS Site Response Manager is responsible for managing the site removal action tasks. This includes managing subcontractors and managing sediment removal, sediment, and restoration.	Associate Construction Management, over 25 years experience
Jackie Doan / Tonya Balla	ERRS Sample Management Coordinator	EQ ERRS/WESTON START	The Sample Management Coordinator is responsible for the procurement of the laboratory and is the main interface with the laboratory regarding project deliverables and QA/QC aspects of the analyses. The OSC, ERRS response manager, and WESTON interface with the laboratory through the Sample Management Coordinator. The Sample Management Coordinator also coordinates sample delivery, and ensures that all analyses are performed and results are delivered on time.	B.S. Chemistry; over 24 years of experience / B.S. Environmental Sampling; over 18 years experience
TBD	ERRS Site Sample Coordinator	EQ ERRS	The Site Sample Coordinator is responsible for the field activities related to sampling. The Site Sample Coordinator interfaces with the Sample Management Coordinator regarding progress of field activities related to sampling requirements and any issues that arise while in the field.	
Jackie Doan	QAPP Preparer	EQM ERRS	The QAPP preparer is responsible for preparing the site-specific QAPP and is in close communication with the Project Manager, Sample Management Coordinator, and QA officer regarding all aspects of project-specific requirements.	B.S. Chemistry; over 24 years of experience
Taryn M. Mancine	Lab PM	Test America Laboratories, Inc.	The Lab Project Manager is responsible for ensuring all laboratories tasks are performed in accordance with this QAPP.	B.S. Forensic Chemistry and Forensic Biology; 2 years of experience

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QAPP Worksheet #8 Special Personnel Training Requirements Table

Project Function	Specialized Training – Title or Description of Course	Training Provider	Training Date	Personnel/Groups Receiving Training	Personnel Titles/ Organizational Affiliation	Location of Training Records/Certificates[1]
Removal Tasks; Field Sampling Activities; and Removal Oversight Activities	40-Hour OSHA HAZWOPER Training and Recurrently Annual 8-hour refreshers	Various	Various	U.S. EPA OSC, EQ ERRS RM, WESTON START Site Leader, WESTON START site personnel, EQM ERRS site personnel and subcontractors working at the site	U.S. EPA, EQ ERRS, WESTON START	WESTON's web-based EHS Track for WESTON START personnel On-site for WESTON START and EQ ERRS personnel

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QAPP Worksheet #9 Project Scoping Session Participants Sheet

Project Name: Portage Creek Area Site **Projected Date(s) of Sampling:** Removal action activities begin in September 2011 **Project Manager:** Eric Bowman, RM	**Site Name:** Portage Creek Area Site **Site Location**: Kalamazoo, Kalamazoo County, Michigan

Date of Session: July 10, 2011
Scoping Session Purpose: Removal Action Approach / Plan Requirements

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
Eric Bowman	Response Manager	EQ	513-265-8875	ebowman@eqm.com	Alternate Response Manager
Jeff Rhinefield	Site Response Manager	EQ	513-309-4703	jrhinefield@eqm.com	Response Manager
Jackie Doan	Director of Quality	EQ	513-673-4210	jdoan@eqm.com	Sample Manager/QA
Todd Valli	Health & Safety Manager	EQ	513-825-7500	tvalli@eqm.com	Health and Safety Manager
Jim Wendle	President	EQ	513-825-7500	jwendle@eqm.com	Corporate Sponsor
Jim Zody	VP Government Contracts	EQ	513-825-7500	jzody@eqm.com	Program Manager
Joe Hoffman	VP Systems	EQ	513-825-7500	jhoffman@eqm.com	EQ System Support
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Mike Arozarena	Engineer	EQ	513-825-7500	marozarena@eqm.com	Permitting Support
Jill Benzer	Scientist	EQ	513-825-7500	jbenzer@eqm.com	Permitting Support
Aziz Omara	Engineer	EQ	219-844-3500	aomara@eqenineers.com	Project Structural Engineer

Comments/Decisions: During scoping session EQ personnel discussed the project approach.

Action Items: EQ ERRS began project plans July 11, 2011

Consensus Decisions: See above.

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QAPP Worksheet #10 Problem Definition

The problem to be addressed by the project:
The Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund site (Superfund Site) includes five disposal areas, five paper mill properties, an approximately 80-mile stretch of the Kalamazoo River from Morrow Dam to Lake Michigan, and a three-mile stretch of Portage Creek. At this time, the site is divided into five cleanup projects known as operable units (OUs):

- OU #1, Allied Paper Property/Bryant Mill Pond Area;
- OU #2, Willow Boulevard and A-Site Landfill;
- OU #3, King Highway Landfill;
- OU #4, 12th Street Landfill; and
- OU #5, the Portage Creek and Kalamazoo River sediments.

The primary site contaminant is polychlorinated biphenyls (PCBs), a hazardous substance and probable human carcinogen. PCBs were introduced to Portage Creek and the Kalamazoo River through past discharges and disposal of PCB-contaminated paper residuals by the paper industry. The five disposal areas are situated on the river banks and contain millions of cubic yards of PCB-contaminated waste. It has been estimated that the river sediments contain more than 120,000 pounds of PCBs. The contaminated sediments have largely been deposited in four impoundment areas.

Between 1954 and the early 1970s, the Superfund Site was used by several paper companies that recycled carbonless copy paper. The recycling process used PCBs, resulting in large amounts of contaminated waste upstream from the Portage Creek Area Site, a portion of OU5 of the Superfund Site. Until 1970, wastewater from the recycling process was released directly into a 29-acre pond within Portage Creek.

The potential for eroding banks and creek channel bottom in the area of Portage Creek from Reed Street to its confluence with the Kalamazoo River may serve as a source of PCBs to the Kalamazoo River. This Time Critical Removal Action (TCRA) has been designed to address the removal and stabilization of targeted creek sediments and floodplain soils in the Portage Creek Area using the Plainwell No. 2 Dam Area Time-Critical Removal Action Final Design Report (ARCADIS BBL, July 2007) as a model. The Portage Creek Area site begins at Reed Street and follows the creek north about three miles to the Kalamazoo. The site is bordered by residential, commercial and industrial properties, as well as undeveloped properties.

This QAPP for the TCRA of contaminated sediment from Portage Creek will be implemented according to the procedures presented in the Portage Creek Removal Work Plan documents (WP), Field Sampling Plan (FSP) and Health and Safety Plan (HASP). The purpose of the TCRA for the Portage Creek Removal effort is to remove the existing polychlorinated biphenyls (PCBs) in soils and sediment of the Portage Creek from Reed Street to the confluence with the Kalamazoo River in Kalamazoo, MI. The section of the Portage Creek Area targeted for action has been divided into 10 distinct Removal Areas within 7 designated Slope Areas (SA1 - SA7) of Portage Creek. Slope Areas are designated by the

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Worksheet #10 – continued

changes in elevation differences, or slope, of the Portage Creek stream bed. The 10 targeted removal areas will be referred to as SA1-A, SA1-B, SA1-C, SA3-A, SA5-A, SA5-C, Axtell Creek, SA5-D, SA6, and SA7. Figure 1 presents an area map. The Removal Areas are presented in Figure 2.

Sampling and analysis activities will be performed for the following:

- Pre-removal PCB soil and sediment concentrations in removal areas that have data gaps.
- Pre- and post-construction conditions of surface soils in support areas.
- Waste characterization of sediments removed.
- Borrow source material sampling.
- Surface soil samples in Upjohn Park.
- Wastewater treatment effluent monitoring.
- Personnel and area monitoring.
- Surface water quality monitoring in the stream.
- Post-excavation soil and sediment conditions (confirmation sampling).

The environmental questions being asked: Will the excavation of sediments from the banks and floodplains of the Portage Creek Area from Reed Street to the confluence with the Kalamazoo River result in statistically lower PCB levels in the fish and animals that inhabit this portion of the Portage Creek and eliminate the imminent and substantial danger to both human and ecological receptors?

The possible classes of contaminants and the affected matrices: The main contaminant of concern is PCBs in soils and sediment. The following identifies the analytes that will be monitored for each matrix:

- Pre-removal soil and sediment concentrations in removal areas that have data gaps - PCBs.
- Pre- and post-construction conditions of surface soils in support areas – target compound list (TCL) volatiles (VOCs), TCL semivolatiles (SVOCs), TCL pesticides, TCL herbicides, PCBs, target analyte list (TAL) metals.
- Waste characterization of sediments removed – toxicity characteristic leaching procedure (TCLP) VOCs, TCLP SVOCs, TCLP Metals, TCLP pesticides, TCLP herbicides, pH, flashpoint, total cyanide (CN), and total sulfide (sulfide).
- Borrow source material sampling – TCL VOCs, TCL SVOCs, TCL Pesticides, TCLP Herbicides, PCBs, and TAL Metals,
- Surface soil samples in Upjohn Park – PCBs.
- Wastewater treatment effluent monitoring – PCBs, Total Suspended Solids (TSS), and phosphorus.
- Personnel and area monitoring – PCBs and total particulates.

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Worksheet #10 – continued

- Surface water quality monitoring in the stream – turbidity, PCBs, TSS, and phosphorus.
- Post-excavation soil and sediment conditions (confirmation sampling) - PCBs.

The rationale for inclusion of chemical and non-chemical analyses: Sampling occurred between 1990 and 2000, several parties responsible for the contamination, including Georgia Pacific LLC and Millennium Holdings, investigated the Portage Creek site under an agreement with the EPA and the state of Michigan. In November 2010, the MDNR collected soil and sediment samples that showed high levels of PCB contamination. PCBs last in the environment because they adhere readily to organic material in sediment and soil and tend to build up in the fatty tissue of fish and other animals. PCBs have been demonstrated to cause a variety of adverse health effects in animals. PCBs cause cancer and noncancer health effects on the immune, reproductive, nervous and endocrine systems. Studies suggest PCBs have similar effects on people. The different health effects of PCBs may be interrelated, as alterations in one system may have significant implications for other systems of the body. The potential adverse environmental and health effects of PCBs were not well understood until 1977, when the government banned most uses of PCBs.

Project decision conditions ("If..., then..." statements):

- If PCBs are detected in the soils and/or sediments in removal areas that have data gaps (see Table 10a and Figures 3 to 9), no action will be taken. Sampling will be performed for information purposes to confirm removal depths.
- If post-construction results indicate support area conditions of surface soils has been impacted by site activities (through comparison of results between pre-construction samples and post-construction samples), further evaluation of extent of contamination may be performed. Surface soils may be removed of and disposed of offsite if necessary.
- If waste characterization analysis of sediments indicates removed sediments are above applicable Resource and Recovery Conservation Act (RCRA) and/or Toxic Substance Control Act (TSCA) limits, material will be disposed of in accordance with applicable regulations.
- If results of samples taken of borrow source material indicates results exceed Michigan Department of Environmental Quality (MDEQ) Part 201 Generic Cleanup Criteria and Screening Levels, Table 2, Residential Direct Contact Criteria and Risk Based Screening Levels (RBSLs) the subject material will not be used as fill material for restoration purposes. Alternate sources of material will be identified and subsequently sampled for the target compounds.
- If surface soil samples in Upjohn Park indicated the presence of PCBs further investigation will be conducted to determine the extent of contamination with the potential for removal of the targeted surface soils.
- If wastewater treatment effluent samples indicate results exceed the MDEQ discharge limits for the compounds of concern (PCBs, TSS and phosphorus) the water will be modified so discharge limits are achieved. In the event samples collected between carbon units indicates in increase in the COCs the potential for carbon saturation will be evaluated with the carbon replaced prior to breakthrough.
- In the event personnel and/or area monitoring results exceed appropriate National Institute for Occupational Safety and Health (NIOSH) Permissible Exposure Limits (PEL), work activities in the vicinity of the sampling area will be ceased and an evaluation of construction

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Worksheet #10 – continued

activities will be performed. Necessary engineering controls maybe implemented to control potential release of compounds of concern. If personnel results approach NIOSH PELs, an evaluation work practices and the required PPE will be conducted. Subsequent sampling will be performed immediately upon work activities resuming.

- Detailed information regarding surface water quality monitoring can be found in Table 10b and Figure 13.
- If Post-excavation soil and sediment conditions (confirmation sampling) exceed the target removal action levels (ALs), additional removal actions will be performed to achieve site cleanup goals and ALs.

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TABLE 10a. PRE-REMOVAL SEDIMENT SAMPLING

Removal Area	Grid	Depth of Samples	No. Cores in Grid	No. of anticipated samples per core
Area 7				
	SA7-4	24 in	2	2
Area 6				
	SA6-1	24 in	1	2
	SA6-6	36 in	1	3
	SA6-10	24 in	1	2
	SA6-11	24 in	1	2
	SA6-14	36 in	2	6
Axtell Creek				
	AXC-1	36 in	1	3
	AXC-3	24 in	1	2
Area 5D				
	SA5-D1	36 in	2	6
	SA5-D2	36 in	1	3
	SA5-D3	36 in	1	3
	SA5-D4	36 in	1	3
	SA5-D7	36 in	1	3
	SA5-D12	48 in	1	4
	SA5-D14	48-60 in	1	4-5
Areas 5C				
	SA5-C2	36 in	1	3
	SA5-C3	36 in	1	3
	SA5-C4	48-60 in	1	4-5
	SA5-C5	48-60 in	1	4-5
Areas 5A				
	SA5-A5	48in	1	4
	SA5-A6	48in	1	4
	SA5-A7	48in	1	4
Area 3A				
	SA3-A1	36 in	1	3
	SA3-A2	36 in	1	3
	SA3-A7	36 in	1	3
Area 1A				
	SA1-A9	36 in	1	3

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Worksheet #10 – continued

TABLE 10b. RESUSPENSION MONITORING

Activity	Location	Location /Type	Parameter	Frequency	Metric
Water Monitoring	200 ft upstream of work area; 300 ft downstream of work area	Grab sample	PCBs TSS Phosphorus	Weekly (phosphorus – monthly)	N/A
Routine Turbidity Monitoring	200 ft upstream of work area; 200 and 300 ft respectively, downstream of work area	Turbidity probe at turbidity station	Turbidity (NTU)	Instantaneous readings conducted at 30 minute intervals	2 times of concurrent upstream value
Supplemental Turbidity Monitoring	Within and outside the resuspension control system as necessary to identify and correct potential problems with the system	Visual surface inspection	Turbidity (NTU)	As required to diagnose potential source of metric exceedance	N/A
Verification that resuspension control system is properly installed	Entire resuspension control system	Visual surface inspection	Integrity, proper function	Once prior to initiation of work at a given work area and as required in the event of any major repair or modification of the resuspension control system	If integrity or function appears compromised, repairs or modifications will be implemented as necessary
Routine resuspension control system inspections during sediment removal work periods	Perimeter of system, at water surface	Inspections	Integrity, proper function	Daily, and as needed to evaluate potential problem conditions	If the integrity or function of the system appears compromised, repairs or modifications will be implemented as necessary

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QAPP Worksheet #11 Project Quality Objectives/Systematic Planning Process Statements

Who will use the data? U.S. EPA Region V, MDEQ, EQ and subcontracted disposal facilities.

What will the data be used for? The data will be used to evaluate successful removal of PCB contaminated sediment and soils of Portage Creek between Reed Street and the confluence with the Kalamazoo River.

What type(s) of data are needed? (target analytes, analytical groups, field screening, on-site analytical or off-site laboratory techniques, sampling techniques):

- Pre-removal soil and sediment concentrations in removal areas that have data gaps - PCBs.
- Pre- and post-construction conditions of surface soils in support areas – TCL VOCs, TCL SVOCs, TCL pesticides, TCL herbicides, PCBs, TAL metals.
- Waste characterization of sediments removed – TCLP VOCs, TCLP SVOCs, TCLP Metals, TCLP pesticides, TCLP herbicides, pH, flashpoint, CN, and sulfide.
- Borrow source material sampling – TCL VOCs, TCL SVOCs, TCL Pesticides, TCLP Herbicides, PCBs, and TAL Metals,
- Surface soil samples in Upjohn Park – PCBs.
- Wastewater treatment effluent monitoring – PCBs, TSS, and phosphorus.
- Personnel and area monitoring – PCBs and total particulates.
- Surface water quality monitoring in the stream – turbidity, PCBs, TSS, and phosphorus.
- Post-excavation soil and sediment conditions (confirmation sampling) - PCBs.

All applicable QC samples (duplicates, blanks, and matrix spikes) will also be collected. An EQ-procured commercial laboratory(s) will be utilized for analytical services for extent of contamination samples and confirmation samples.

How "good" do the data need to be in order to support the environmental decision? The data will need to be defensible and will therefore all be conducted off-site by commercial laboratories utilizing appropriate methodology.

How much data are needed? (number of samples for each analytical group, matrix, and concentration):

See Table 11a for number of samples for each matrix.

All applicable QC samples (duplicates and matrix spikes) will also be collected.

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Worksheet #11 – continued

Where, when, and how should the data be collected/generated? Samples will be collected from the pre-established locations in the Portage Creek, see Figures 3-9.

Who will collect and generate the data? EQ and Weston START will collect the data. The analytical data will be generated by two laboratories. The samples will be analyzed by Test America Laboratories, Inc. in Dayton, Ohio; Savannah, Georgia; and Phoenix, Arizona. The Phoenix facility will analyze the air samples, Savannah will analyze for herbicides and sulfide, and the Dayton facility will analyze all other samples.

How will the data be reported? The laboratories will submit a summary report to the EQ Sample Management Coordinator by e-mail. The summary report will include sample results, QC summary results, and a chain of custody. The EQ Sample Management Coordinator will distribute the summary report to the U.S. EPA OSC, who will in turn distribute the summary report to interested parties internally. The summary report will not be distributed further until the data has been reviewed and validated by an EQ or START chemist.
A final data package will be provided in a pdf format. All data with the exception of waste characterization results will be reported in a final data package that will include the information presented in the summary report along with sample extraction information, calibration (initial and continuing), standard preparation logs, all associated instrument outputs. This final data package will be accompanied by an electronic data deliverable (EDD) formatted in accordance with Laboratory Data Consultants' (LDCs) automated data reporting (ADR) tool and the project specific electronic QAPP.

How will the data be archived? EQ will maintain a copy of all site-related data and files for a period of 10 years in accordance with its policies. In addition, EQ will send a copy of all data to the U.S. EPA's records center.

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Worksheet #11 – continued

TABLE 11a. SAMPLING SCHEME

Location	Matrix	Purpose	Number of Samples /SU[1]	Total Number of SU	SU Locations	Total Number of Samples[2]	Sampling Method
Targeted Grids from each Slope Area	Sediment and soil	confirm sediment removal depth for grid with data gaps	2-5	26	See Figures 3 to 9	110-113	sediment/soil core composite
Targeted Removal Area	Sediment and soil	waste characterization to complete profile for disposal	4	2-3	9	TBD	sediment/soil core composite
Upjohn Park	soil	Potential extent of contamination	1	12-20	TBD	TBD	surface grab
Construction Area	soil	pre-construction & post-construction conditions	6	1/2500 sf	Support Areas[3]	TBD	surface soil composite
Source Material	solids	confirm backfill is clean prior to placement	1	1/5000 cy	TBD	TBD	composite
Turbidity Monitoring Stations	surface water	water quality monitoring	1	3	200 ft upstream, 200 ft and 300 ft downstream	1 measurement each location every 30 minutes	Real Time Measurements - Turbidity
Turbidity Monitoring Stations	surface water	water quality monitoring	1	2	200 ft upstream, 200 ft and 300 ft downstream	2	grab
Personnel Workers within exclusion zone	air	personnel monitoring	1	1 worker	breathing zone of workers in removal/staging areas	TBD	NIOSH 5503
Work Area	air	area monitoring	5	1	2 locations upwind, 3 locations downwind of work area	multiple	real time measurement – DataRam
Perimeter Monitoring	air	confirm no release of contaminants from work areas	1	5	2 locations upwind, 3 locations downwind of removal area	5/day for each day of processing activities	NIOSH 5503
Wastewater treatment	waste water	confirm removal of contaminants prior to discharge	1	3	influent, mid-GAC, effluent	3	grab
Removal Grid Areas	sediment	Confirm removal of PCB contaminated sediment	6	72	See Figures 3 to 9	72	sediment core composite
Removal Grid Areas	sediment	statistical analysis of project objectives	6	8	TBD	48	grab

Notes:
1. SU – sampling unit such as a slope area removal grid or each 2500 sf of construction areas.
2. Does not include QC samples.
3. Command Post, dewatering/staging areas, waste water treatment plant, truck wash.
4. TBD – to be determined based on site conditions

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QAPP Worksheet #12 Measurement Performance Criteria Table

Worksheet 12-1

Matrix	Surface Water and Waste Water
Analytical Group	TSS, PCB and Total Phosphorus
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
• Weekly grab sample 200 ft upstream and 300 ft downstream from active excavation area • weekly grab of influent, mid-stream and effluent samples from the water treatment system.	2540D/ DT-WET-029.1 4500P / DT-WET-056.1 608/ DT-ORG-002.1	1. Precision 2. Accuracy 3. Representativeness 4. Comparability 5. Completeness 6. Sensitivity	1. RPD 2. %R 3. Qualitative 4. Qualitative 5. % expected sample points, % expected results of samples 6. Reporting Limit	1. Field Duplicate, MSD 2. LCS, MS 3. Field blanks, & dups 4. NA 5. Data completeness check 6. Comparison to Regulatory Threshold	1. S&A 2. S&A 3. S 4. S&A 5. S&A 6. A

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Worksheet #12 – continued

QAPP Worksheet #12 Measurement Performance Criteria Table

Worksheet 12-2

Matrix	Sediment (Confirmation)
Analytical Group	PCB
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
One six-point composite sample taken from each of the pre-established grids.	SW846 8082/ DT-ORG-017.1	1. Precision 2. Accuracy 3. Representativeness 4. Comparability 5. Completeness 6. Sensitivity	1. RPD 2. %R 3. Qualitative 4. Qualitative 5. % expected sample points, % expected results of samples 6. Reporting Limit	1. Field Duplicate, MSD 2. LCS, MS 3. Field blanks, & dups 4. NA 5. Data completeness check 6. Comparison to Regulatory Threshold	1. S&A 2. S&A 3. S 4. S&A 5. S&A 6. A

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Worksheet #12 – continued

Worksheet 12-3

Matrix	Sediment (Pre-Removal/Data Gaps)
Analytical Group	PCB
Concentration Level	Medium

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
To address data gaps one composite sediment core sample per pre-established gird. Cores will be taken to the maximum excavation depth. One sample per 12 inches of each core.	SW846 8082/ DT-ORG-017.1	1. Precision 2. Accuracy 3. Representativeness 4. Comparability 5. Completeness 6. Sensitivity	1. RPD 2. %R 3. Qualitative 4. Qualitative 5. % expected sample points, % expected results of samples 6. Reporting Limit	1. Field Duplicate, MSD 2. LCS, MS 3. Field blanks, & dups 4. NA 5. Data completeness check 6. Comparison to Regulatory Threshold	1. S&A 2. S&A 3. S 4. S&A 5. S&A 6. A

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Worksheet #12 – continued

QAPP Worksheet #12-4

Matrix	Sediment/Soil (to be Removed)
Analytical Group	Waste Characterization - TCLP (VOCs, SVOCs, Pesticides, Herbicides, RCRA Metals), PCBs, Total Cyanide and Sulfide, Flashpoint, pH and Paint Filter
Concentration Level	High

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
One composite sample per Removal Area. Composites can be generated using cores taken from pre-removal sampling or random grab samples taken prior to removal. Samples are to address sediments up to the targeted removal depth.	SW846 1311/DT-ORG-003.2 SW846 8260/DT-ORG-007.1 SW846 8270/DT-ORG-008.1 SW846 6010B/ DT-MET-016.0 SW846 7470/DT-MET-018.2 SW846 8081/DT-ORG-015.1 SW846 8151/SOP Herbicides SAV SW846 9012/DT-WET-060.1 SW846 9034/SOP Sulfide soil SAV SW846 1010/DT-WET-015.1 SW846 9045/DT-WET-019.1 SW846 9095/DT-WET-020.1	1. Precision 2. Accuracy 3. Representativeness 4. Comparability 5. Completeness 6. Sensitivity	1. RPD 2. %R 3. Qualitative 4. Qualitative 5. % expected sample points, % expected results of samples 6. Reporting Limit	1. Lab Duplicate, MSD 2. LCS, MS 3. Field blanks, & dups 4. NA 5. Data completeness check 6. Comparison to Regulatory Threshold	1. S&A 2. S&A 3. S 4. S&A 5. S&A 6. A

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Worksheet #12 – continued

QAPP Worksheet #12-5

Matrix	Soil (Staging/Support Areas Pre- and Post-Construction)
Analytical Group	VOCs, SVOCs, Metals, Pesticides/PCB, Herbicides
Concentration Level	Medium

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
1 six-point composite sample collected per 2500 SF of staging area for PCBs. One composite of 4 grids for remaining parameters.	SW846 8260/DT-ORG-007.1 SW846 8270/DT-ORG-008.1 SW846 6010B/DT-MET-016.0 SW846 6020A/DT-MET-024.1 SW846 7470/DT-MET-018.2 SW846 8081/DT-ORG-015.1 SW846 8082/DT-ORG-017.1 SW846 8151/SOP Herbicides SAV	1. Precision 2. Accuracy 3. Representativeness 4. Comparability 5. Completeness 6. Sensitivity	1. RPD 2. %R 3. Qualitative 4. Qualitative 5. % expected sample points, % expected results of samples 6. Reporting Limit	1. Field Duplicate, MSD 2. LCS, MS 3. Field blanks, & dups 4. NA 5. Data completeness check 6. Comparison to Regulatory Threshold	1. S&A 2. S&A 3. S 4. S&A 5. S&A 6. A

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Worksheet #12 – continued

QAPP Worksheet #12-6

Matrix	Borrow Source - Backfill (Gravel, soil, and Sand)
Analytical Group	VOCs, SVOCs, Metals, Pesticides/PCB, Herbicides
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
Six point composite samples using dedicated disposal sampling device or coring device. One sample for each 5000 cubic yards of each material from each source.	SW846 8260/DT-ORG-007.1 SW846 8270/DT-ORG-008.1 SW846 6010B/DT-MET-016.0 SW846 6020A/DT-MET-024.1 SW846 7470/DT-MET-018.2 SW846 8081/DT-ORG-015.1 SW846 8082/DT-ORG-017.1 SW846 8151/SOP Herbicides SAV	1. Precision 2. Accuracy 3. Representativeness 4. Comparability 5. Completeness 6. Sensitivity	1. RPD 2. %R 3. Qualitative 4. Qualitative 5. % expected sample points, % expected results of samples 6. Reporting Limit	1-2. Lab Duplicate and Spike Duplicate 3-4. Sample Preparation 5. Data completeness check 6. Comparison to Regulatory Threshold	1. S&A 2. S&A 3. S 4. S&A 5. S&A 6. A

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Worksheet #12 – continued

QAPP Worksheet #12-7

Matrix	Air
Analytical Group	PCB and Particulates
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
Composite sample of personnel breathing zone for workers within Exclusion Zone as well as monitoring of the excavation and staging areas during excavation and solidification.	NIOSH 5503/SOP 5503 PHX NIOSH 0500/SOP 0500 PHX	1. Precision 2. Accuracy 3. Representativeness 4. Comparability 5. Completeness 6. Sensitivity	1. RPD 2. %R 3. Qualitative 4. Qualitative 5. % expected sample points, % expected results of samples 6. Reporting Limit	1. NA 2. LCS 3. Field Blank 4. NA 5. Data completeness check 6. Comparison to Regulatory Threshold	1. S&A 2. S&A 3. S 4. S&A 5. S&A 6. A

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QAPP Worksheet #13 Secondary Data Criteria and Limitations Table

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Org., Data Types, Data Generation/Collection Dates)	How Data Will Be Used	Limitations on Data Use
Fields (2011a)	USEPA Field Environmental Decision Support. 2011a. *Portage Creek Remediation: Volume and Mass Estimations.* 14 April.	USEPA Field Environmental Decision Support	Targeted removal depths and PCB sediment concentrations will guide removal actions	Data gaps exists in certain removal grids

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QAPP Worksheet #14 Summary of Project Tasks

Sampling Tasks:

Sampling and analysis activities will be performed for the following:

- Pre-removal PCB soil and sediment concentrations in removal areas that have data gaps.
- Pre- and post-construction conditions of surface soils in support areas.
- Waste characterization of sediments removed.
- Borrow source material sampling.
- Surface soil samples in Upjohn Park.
- Wastewater treatment effluent monitoring.
- Personnel and area monitoring.
- Surface water quality monitoring in the stream.
- Post-excavation soil and sediment conditions (confirmation sampling).

Analysis Tasks:

The ERRS-procured commercial laboratory, Test America Laboratory in Phoenix, Arizona will prepare and process air samples, Savannah will process samples for herbicides and sulfide analysis and the Dayton, Ohio facility will prepare and process all other samples for analysis.

Quality Control Tasks:

1. Collect field duplicate and blank samples per QAPP.
2. Perform sample collection procedures per QAPP.
3. Laboratories to perform laboratory QC procedures. QC procedures include analyzing blanks, laboratory control sample, and matrix spike/matrix spike duplicate samples.
4. ERRS or START Chemist to provide data validation of analytical reports from laboratory.

Secondary Data:

USEPA Field Environmental Decision Support. 2011a. *Portage Creek Remediation: Volume and Mass Estimations.* 14 April.

Weston Solutions, Inc. (Weston). 2011. *Detailed cost Estimate for Removal of Contaminated Sediments in Portage Creek Kalamazoo, Kalamazoo County, Michigan.* 13 April

Data Management Tasks:

Data will be evaluated against the applicable project action levels.

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Worksheet #14 – continued

Documentation and Records:
Sampling locations will be documented and all sample collection data will be recorded in field logbooks and/or field sampling logs. COCs and sample logs will be prepared and retained for each sample. A copy of all finalized documents and analytical data will be retained in a central file area.

Assessment/Audit Task:
Assessment of field activities will be carried out by the Project Manager through daily contact with the site leader. Audits will be carried out as directed and approved by the OSC. At this time no audits have been scheduled to occur at the Site.

Data Review Tasks:
The laboratory will review all analytical data for completeness and quality. The analytical data will then be submitted to the U.S. EPA's ERRS or START contractor for distribution to the U.S. EPA OSC. The analytical data will be reviewed and validated by an ERRS or START Chemist. The final qualified data results and data validation report will be submitted to the U.S. EPA OSC upon completion. This will be accomplished in accordance with the laboratories quality management plan and internal policies. A case narrative describing any quality control issues with the analyses will be submitted with the final data report. In addition, the laboratory will qualify data in accordance with its quality policies. EQM will provide a data compliance check of all data received prior to utilizing in any report.

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QAPP Worksheet #15 Reference Limits and Evaluation Table

UFP QAPP Worksheet #15-1
Matrix: Wastewater Effluent
Analytical Group: TSS (SM2540D), PCB (EPA 608) and Total Phosphorus (SM4500P)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (mg/L)	Test America MDL (mg/L)	Test America RL (mg/L)
TSS	-	-	5.00	5.00
Total Phosphorus	7723-14-0	-	0.0474	0.100
Total PCB	-	0.200 ug/L	0.0614 ug/L	0.200 ug/L

The laboratory will be reporting to the MDL for PCBs.

UFP QAPP Worksheet #15-2
Matrix: Sediment- Confirmation Samples
Analytical Group: PCB (SW846 8082)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (mg/kg)	Test America MDL (mg/kg)	Test America RL (mg/kg)
PCB-1016	12674-11-2	*	0.0164	0.100
PCB-1221	11104-28-2	*	0.0423	0.100
PCB-1232	11141-16-5	*	0.00800	0.100
PCB-1242	53469-21-9	*	0.0220	0.100
PCB-1248	12672-29-6	*	0.0111	0.100
PCB-1254	11097-69-1	*	0.0228	0.100
PCB-1260	11096-82-5	*	0.0156	0.100

*The performance standard for stream sediments is ≤ 10 mg/kg with a performance standard goal of 1 mg/kg.
*The performance standard for floodplain and bank soils is 10 mg/kg with a performance standard goal of 5 mg/kg.

UFP QAPP Worksheet #15-3
Matrix: Sediment- Pre-Removal/Data Gaps
Analytical Group: PCB (SW846 8082)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit (mg/kg)	Test America MDL (mg/kg)	Test America RL (mg/kg)
PCB-1016	12674-11-2	*	0.0164	0.100
PCB-1221	11104-28-2	*	0.0423	0.100
PCB-1232	11141-16-5	*	0.00800	0.100
PCB-1242	53469-21-9	*	0.0220	0.100
PCB-1248	12672-29-6	*	0.0111	0.100
PCB-1254	11097-69-1	*	0.0228	0.100
PCB-1260	11096-82-5	*	0.0156	0.100

*Results will be used for information purposes only

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Worksheet #15 – continued

UFP QAPP Worksheet #15-4
Matrix: Solid
Analytical Group: Waste Characterization TCLP (SW846)
Concentration Level: High

Analyte	CAS Number	Project Action Limit (mg/L)	Test America MDL (mg/L)	Test America RL (mg/L)
Arsenic	7440-38-2	5.0	0.0356	0.500
Barium	7440-39-3	100.0	0.00850	1.00
Benzene	71-43-2	0.5	0.000456	0.00100
Cadmium	7440-43-9	1.0	0.00348	0.150
Carbon Tetrachloride	56-23-5	0.5	0.000439	0.00100
Chlorobenzene	108-90-7	100.0	0.000450	0.00100
Chloroform	67-66-3	6.0	0.000481	0.00100
Chromium	7440-47-3	5.0	0.00781	0.200
o-Cresol	95-48-7	200.0	0.0230	0.100
m-Cresol[1]	108-39-4	200.0	0.0220	0.100
p-Cresol[1]	106-44-5	200.0	0.0220	0.100
1,4-Dichlorobenzene	106-446-7	7.5	0.0310	0.100
1,2-Dichloroethane	107-06-2	0.5	0.000534	0.00100
1,1-Dichloroethylene	75-35-4	0.7	0.000451	0.00100
2,4-Dinitrotoluene	121-14-2	0.13	0.0209	0.100
Hexachlorobenzene	118-74-1	0.13	0.0162	0.100
Hexachlorobutadiene	87-68-3	0.5	0.0360	0.100
Hexachloroethane	67-72-1	3.0	0.0340	0.100
Lead	7439-92-1	5.0	0.0221	0.400
Mercury	7439-97-6	0.2	0.000160	0.00100
Methyl ethyl ketone	78-93-3	200.0	0.00208	0.0125
Nitrobenzene	98-95-3	2.0	0.0240	0.100
Pentachlorophenol	87-86-5	100.0	0.0769	0.100
Pyridine	110-86-1	5.0	0.0287	0.100
Selenium	7782-49-2	1.0	0.0740	0.500
Silver	7440-22-4	5.0	0.00703	0.200
Tetrachloroethylene	127-18-4	0.7	0.000450	0.00100
Trichloroethylene	79-01-6	0.5	0.000453	0.00100
2,4,5-Trichlorophenol	95-95-4	400.0	0.0493	0.100
2,4,6-Trichlorophenol	88-06-2	2.0	0.0626	0.100
Vinyl chloride	75-01-4	0.2	0.000540	0.00100

[1] Will be reported as 3,4-methylphenol

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Worksheet #15 – continued

UFP QAPP Worksheet #15-5
Matrix: Solid
Analytical Group: Waste Characterization Wet Chem (SW846)
Concentration Level: High

Analyte	CAS Number	Project Action Limit (mg/kg)	Test America MDL (mg/kg)	Test America RL (mg/kg)
Total Cyanide	-	250	0.163	0.25
Reactive Sulfide	-	500	0.2	5
Flashpoint	-	60°C	-	25°C
pH	-	2-12	0.1 (SU)	0.1 (SU)

°C – degrees Celsius
SU- Standard Unit

UFP QAPP Worksheet #15-6
Matrix: Air
Analytical Group: Worker Exposure Assessment (PCB by NIOSH 5503)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (mg/m^3)	Test America MDL (µg/sample)	Test America RL (µg/sample)
PCB-1016	12674-11-2	0.5	0.0147	0.100
PCB-1221	11104-28-2	0.5	0.100	0.100
PCB-1232	11141-16-5	0.5	0.100	0.100
PCB-1242	53469-21-9	0.5	0.100	0.100
PCB-1248	12672-29-6	0.5	0.100	0.100
PCB-1254	11097-69-1	0.5	0.100	0.100
PCB-1262	37324-23-5	0.5	0.100	0.100
PCB-1260	11096-82-5	0.5	0.0127	0.100

UFP QAPP Worksheet #15-7
Matrix: Air
Analytical Group: Worker Exposure Assessment (Particulates by NIOSH 0500)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (mg/m^3)	Test America MDL (µg/sample)	Test America RL (µg/sample)
Particulates	-	15	38	100

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Worksheet #15 – continued

U**FP QAPP Worksheet #15-8**
Matrix: Solid
Analytical Group: Pre- and Post-Construction Staging/Support Areas Metals (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (mg/kg)	Test America MDL (mg/kg)	Test America RL (mg/kg)
Aluminum	7429-90-5		4.05	16.6
Antimony	7440-36-0		0.0492	0.200
Arsenic	7440-38-2		1.04	16.6
Barium	7440-39-3		0.144	3.33
Beryllium	7440-41-7		0.126	0.835
Cadmium	7440-43-9		0.173	5.00
Calcium	7440-70-2		5.26	166
Chromium	7440-47-3		0.148	6.65
Cobalt	7440-48-4		0.282	3.33
Copper	7440-50-8		0.0456	1.00
Iron	7439-89-6		5.50	16.6
Lead	7439-92-1		1.60	13.3
Magnesium	7439-95-4		1.66	166
Manganese	7439-96-5		0.0459	1.00
Mercury	7439-97-6		0.000300	0.00833
Nickel	7440-02-0		0.366	1.66
Potassium	7440-09-7		4.72	166
Selenium	7782-49-2		1.99	16.6
Silver	7440-22-4		0.0308	0.100
Sodium	7440-23-5		102	166
Thallium	7440-28-0		0.0412	0.200
Vanadium	7440-62-2		0.316	8.35
Zinc	7440-66-6		0.872	8.35

*Pre construction levels will be used in evaluating the post-construction results

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Worksheet #15 – continued

U**FP QAPP Worksheet #15-9**
Matrix: Solid
Analytical Group: Pre- and Post-Construction Staging/Support Areas SVOC (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
Acenaphthene	83-32-9		16.8	147
Acenaphthylene	208-96-8		15.6	147
Acetophenone	98-86-2		28.3	147
2-Acetylaminofluorene	53-96-3		42.0	660
4-Aminobiphenyl	92-67-1		46.0	660
Aniline	62-53-3		15.2	294
Anthracene	120-12-7		50	495
Benzo (a) anthracene	56-55-3		7.89	147
Benzo (b) fluoranthene	205-99-2		17.5	147
Benzo (g,h,i) perylene	191-24-2		12.3	147
Benzo (k) fluoranthene	207-08-9		11.9	147
Benzo (a) pyrene	50-32-8		11.6	147
Benzidine	92-87-5		16.7	1470
Benzyl alcohol	100-51-6		19.9	294
Bis(2-chloroethoxy)methane	111-91-1		24.1	147
Bis(2-chloroethyl)ether	111-44-4		30.7	147
Bis(2-chloroisopropyl) ether	108-60-1		27.1	147
Bis(2-ethylhexyl)phthalate	117-81-7		84.5	147
4-Bromophenyl phenyl ether	101-55-3		23.1	147
Butyl benzyl phthalate	85-68-7		37.6	147
Carbazole	86-74-8		27.6	147
4-Chloroaniline	106-47-8		17.7	147
Chlorobenzilate	510-15-6		43.0	660
4-Chloro-3-methlyphenol	59-50-7		14.9	294
2-Chloronaphthalene	91-58-7		22	147
2-Chlorophenol	95-57-8		26.7	294
4-Chlorophenyl phenyl ether	7005-72-3		27.8	147
Chrysene	218-01-9		8.97	147
Diallate	2303-16-4		47.0	990
Dibenzofuran	132-64-9		27	147
1,2-Dichlorobenzene	95-50-1		32.3	147
1,3-Dichlorobenzene	541-73-1		24	147
1,4-Dichlorobenzene	106-46-7		29.5	147
Dibenz (a,h) anthracene	53-70-3		12.0	147
Di-n-butyl phthalate	84-74-2		62.6	147
3,3'-Dichlorobenzidine	91-94-1		102	1470
2,4-Dichlorophenol	120-83-2		23.5	294
2,6-Dichlorophenol	87-65-0		27.6	294
Diethyl phthalate	84-66-2		31.9	147
7,12-Dimethylbenz (a) anthracene	57-97-6		41.0	660
Dimethoate	60-51-5		48.0	660
Dimethylaminoazobenzene	60-11-7		37.0	660
3,3'-Dimethylbenzidine	119-93-7		62.0	660

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Worksheet #15 – continued

Worksheet 15-9 – Support Areas SVOCs

Analyte	CAS Number	Project Action Limit* (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
2,4-Dimethylphenol	105-67-9		21	294
Dimethyl phthalate	131-11-3		39.5	147
1,3-Dinitrobenzene	99-65-0		24.9	147
4,6-Dinitro-2-methylphenol	534-52-1		18.4	294
2,4-Dinitrophenol	51-28-5		32.6	588
2,4-Dinitrotoluene	121-14-2		17.9	147
2,6-Dinitrotoluene	606-20-2		18.9	147
Di-n-octyl phthalate	117-84-0		32.3	147
Diphenylamine	122-39-4		34.1	660
Disulfoton	298-04-4		44.0	660
Ethyl methanesulfonate	62-50-0		40.0	660
Famphur	52-85-7		63.0	330
Fluoranthene	206-44-0		12.2	147
Fluorene	86-73-7		17.2	147
Hexachlorobenzene	118-74-1		25.3	147
Hexachlorobutadiene	87-68-3		15.7	147
Hexachlorocyclopentadiene	77-47-4		19.1	588
Hexachloroethane	67-72-1		24.2	147
Hexachloropropene	1888-71-7		56.0	990
Indeno (1,2,3-cd) pyrene	193-39-5		11.8	147
Isodrin	465-73-6		43.0	990
Isophorone	78-59-1		28.7	147
Isosafrole	120-58-1		46.0	660
Kepone	143-50-0		280	7500
Methapyrilene	91-80-5		16.0	660
3-Methylcholanthrene	56-49-5		41.0	990
Methyl methane sulfonate	66-27-3		47.0	660
2-Methylnaphthalene	91-57-6		19.9	147
2-Methylphenol (o-Cresol)	95-48-7		28.3	294
3&4-Methylphenol (m&p Cresol)	-		34.5	294
Naphthalene	91-20-3		15.5	147
1,4-Naphthoquinone	130-15-4		64.0	660
1-Naphthylamine	134-32-7		46.0	990
2-Naphthylamine	91-59-8		23.0	990
2-Nitroaniline	88-74-4		31.5	294
3-Nitroaniline	99-09-2		19.4	294
4-Nitroaniline	100-01-6		22.8	294
Nitrobenzene	98-95-3		29.8	147
2-Nitrophenol	88-75-5		31	294
4-Nitrophenol	100-02-7		20.3	294
5-Nitro-o-toluidine	99-55-8		39.0	660
N-Nitrosodi-n-butylamine	924-16-3		46.0	660
N-Nitrosodiethylamine	55-18-5		44.0	990
N-Nitrosodimethylamine	62-75-9		13.7	147
N-Nitrosomethylethylamine	10595-95-6		54.0	660

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Worksheet #15 – continued

Worksheet 15-9 – Support Areas SVOCs

Analyte	CAS Number	Project Action Limit* (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
N-Nitrosodiphenylamine	86-30-6		27.1	147
N-Nitrosodi-n-propylamine	621-64-7		29.7	147
N-Nitrosomorpholine	59-89-2		46	660
N-Nitrosopiperidine	100-75-4		42.0	660
N-Nitropyrrolidine	930-55-2		45.0	660
Parathion-methyl	298-00-0		49.0	660
Parathion	-		44.0	660
Pentachlorobenzene	608-93-5		48.0	660
Pentachlorophenol	87-86-5		27.8	294
Pentachloronitrobenzene	82-68-8		43.0	660
Phenacetin	62-44-2		37.0	660
Phenanthrene	85-01-8		12.2	147
Phenol	108-95-2		33.7	294
1,4-Phenylenediamine	106-50-3		353	990
Phorate	298-02-2		42.0	660
2-Picoline	109-06-8		52.0	660
Pronamide	23950-58-5		43.0	660
Pyrene	129-00-0		15.5	147
Pyridine	110-86-1		58.3	147
Safrole	94-59-7		46.0	660
Sulfotepp	3689-24-5		45.0	660
1,2,4,5-Tetrachlorobenzene	95-94-3		47.0	660
Thionazin	297-97-2		44.0	660
o-Toluidine	95-53-4		42.0	660
2,3,4,6-Tetrachlorophenol	58-90-2		41.0	660
1,2,4-Trichlorobenzene	120-82-1		16.9	147
2,4,5-Trichlorophenol	95-95-4		28.2	294
2,4,6-Trichlorophenol	88-06-2		20	294
O,O,O-Triethyl phosphorothioate	126-68-1		52.0	660
1,3,5-Trinitrobenzene	99-35-4		41.0	990

*Pre construction levels will be used in evaluating the post-construction results

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Worksheet #15 – continued

UFP QAPP Worksheet #15-10
Matrix: Solid
Analytical Group: Pre- and Post-Construction Staging/Support Areas VOCs (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
Acetone	67-64-1		9.03	100
Acrolein	107-02-8		12.9	50.0
Acrylonitrile	107-13-1		1.77	5.00
Allyl chloride	107-05-1		1.51	5.00
Benzene	71-43-2		1.32	5.00
Bromodichloromethane	75-27-4		1.52	5.00
Bromoform	75-25-2		1.57	5.00
Bromomethane (Methyl bromide)	74-83-9		1.29	10.0
2-Butanone (MEK)	78-93-3		3.98	50.0
Carbon disulfide	75-15-0		1.28	5.00
Carbon tetrachloride	56-23-5		1.39	5.00
Chlorobenzene	108-90-7		1.31	5.00
Chloroethane	75-00-3		1.41	5.00
Chloroform	67-66-3		1.18	5.00
Chloromethane (Methyl chloride)	74-87-3		1.28	5.00
Chloroprene	126-99-8		1.33	5.00
Dibromochloromethane	124-48-1		1.49	5.00
1,2-Dibromo-3-chloropropane	96-12-8		1.76	5.00
1,2-Dibromoethane (EDB)	106-93-4		1.43	5.00
Dibromomethane	74-95-3		1.64	5.00
trans-1,4-Dichloro-2-butene	110-57-6		2.02	5.00
1,2-Dichlorobenzene	95-50-1		1.91	5.00
1,4-Dichlorobenzene	106-46-7		1.27	5.00
1,3-Dichlorobenzene	541-73-1		1.90	5.00
Dichlorodifluoromethane	75-71-8		1.10	5.00
1,1-Dichloroethane	75-34-3		1.09	5.00
1,2-Dichloroethane	107-06-2		1.40	5.00
trans-1,2-Dichloroethene	156-60-5		1.34	5.00
1,2-Dichloroethene (total)	540-59-0		1.55	5.00
1,1-Dichloroethene	75-35-4		1.55	5.00
1,2-Dichloropropane	78-87-5		1.35	5.00
cis-1,3-Dichloropropene	10061-01-5		1.31	5.00
1,3-Dichloropropene (total)	NA		1.37	5.00
trans-1,3-Dichloropropene	10061-02-6		1.37	5.00
Ethylbenzene	100-41-4		1.37	5.00
Hexachlorobutadiene	87-68-3		1.63	5.00
Ethyl methacrylate	97-63-2		1.65	5.00
2-Hexanone	591-78-6		4.64	50.0
Iodomethane	74-88-4		1.18	5.00
Methacrylonitrile	126-98-7		1.93	5.00
Methylene chloride	75-09-2		4.94	10.0
Methyl methacrylate	80-62-6		1.60	5.00

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Worksheet #15 – continued

Worksheet 15-10 – Support Areas VOCs

Analyte	CAS Number	Project Action Limit* (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
4-Methyl-2-pentanone (MIBK)	108-10-1		4.77	50
Pentachloroethane	76-01-7		1.22	5.00
Propionitrile	107-12-0		7.54	50.0
Styrene	100-42-5		1.45	5.00
1,1,1,2-Tetrachloroethane	630-20-6		1.27	5.00
1,1,2,2-Tetrachloroethane	79-34-5		1.61	5.00
Tetrachloroethene	127-18-4		1.44	5.00
Toluene	108-88-3		1.35	5.00
1,2,4-Trichlorobenzene	120-82-1		2.37	5.00
1,1,1-Trichloroethane	71-55-6		1.37	5.00
1,1,2-Trichloroethane	79-00-5		1.47	5.00
Trichloroethene	79-01-6		1.29	5.00
Trichlorofluoromethane	75-69-4		1.43	5.00
1,2,3-Trichloropropane	96-18-4		1.70	5.00
Vinyl Acetate	108-05-4		1.40	5.00
Vinyl chloride	75-01-4		1.52	2.00
m,p-Xylene	1330-20-7		2.36	5.00
o-Xylene			1.29	5.00
Xylenes, total	1330-20-7		2.36	5.00

*Pre construction levels will be used in evaluating the post-construction results

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Worksheet #15 – continued

UFP QAPP Worksheet #15-11
Matrix: Solid
Analytical Group: Pre- and Post-Construction Staging/Support Areas VOCs (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (ug/L)	Test America MDL (ug/L)	Test America RL (ug/L)
Acetone	67-64-1		6.25	20.0
Acrolein	107-02-8		22.8	50.0
Acrylonitrile	107-13-1		1.72	5.00
Allyl chloride	107-05-1		0.438	5.00
Benzene	71-43-2		0.456	1.00
Bromodichloromethane	75-27-4		0.402	1.00
Bromoform	75-25-2		0.411	1.00
Bromomethane (Methyl bromide)	74-83-9		0.645	5.00
2-Butanone (MEK)	78-93-3		2.08	12.0
Carbon disulfide	75-15-0		0.446	1.00
Carbon tetrachloride	56-23-5		0.439	1.00
Chlorobenzene	108-90-7		0.450	1.00
Chloroethane	75-00-3		0.446	5.00
Chloroform	67-66-3		0.481	1.00
Chloromethane (Methyl chloride)	74-87-3		0.490	5.00
Chloroprene	126-99-8		0.405	5.00
Dibromochloromethane	124-48-1		0.457	1.00
1,2-Dibromo-3-chloropropane	96-12-8		1.47	5.00
1,2-Dibromoethane (EDB)	106-93-4		0.444	5.00
Dibromomethane	74-95-3		0.488	5.00
trans-1,4-Dichloro-2-butene	110-57-6		2.02	5.00
1,2-Dichlorobenzene	95-50-1		0.503	1.00
1,4-Dichlorobenzene	106-46-7		0.435	1.00
1,3-Dichlorobenzene	541-73-1		0.424	1.00
Dichlorodifluoromethane	75-71-8		0.800	1.00
1,1-Dichloroethane	75-34-3		0.468	1.00
1,2-Dichloroethane	107-06-2		0.534	1.00
trans-1,2-Dichloroethene	156-60-5		0.449	1.00
1,2-Dichloroethene (total)	540-59-0		1.55	2.00
1,1-Dichloroethene	75-35-4		0.451	1.00
1,2-Dichloropropane	78-87-5		0.467	1.00
cis-1,3-Dichloropropene	10061-01-5		0.467	1.00
1,3-Dichloropropene (total)	NA		1.37	2.00
trans-1,3-Dichloropropene	10061-02-6		0.638	1.00
Ethylbenzene	100-41-4		0.419	1.00
Hexachlorobutadiene	87-68-3		0.938	5.00
Ethyl methacrylate	97-63-2		0.525	5.00
2-Hexanone	591-78-6		2.85	10.0
Iodomethane	74-88-4		0.503	5.00
Methacrylonitrile	126-98-7		0.572	5.00
Methylene chloride	75-09-2		0.528	2.00
Methyl methacrylate	80-62-6		0.534	5.00
4-Methyl-2-pentanone (MIBK)	108-10-1		1.53	10.0

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Worksheet #15 – continued

Worksheet 15-11 – Support Areas VOCs

Analyte	CAS Number	Project Action Limit* (ug/L)	Test America MDL (ug/L)	Test America RL (ug/L)
Pentachloroethane	76-01-7		0.439	5.00
Propionitrile	107-12-0		4.10	50.0
Styrene	100-42-5		0.485	1.00
1,1,1,2-Tetrachloroethane	630-20-6		0.485	1.00
1,1,2,2-Tetrachloroethane	79-34-5		0.953	1.00
Tetrachloroethene	127-18-4		0.450	1.00
Toluene	108-88-3		0.522	1.00
1,2,4-Trichlorobenzene	120-82-1		1.31	5.00
1,1,1-Trichloroethane	71-55-6		0.426	1.00
1,1,2-Trichloroethane	79-00-5		0.643	1.00
Trichloroethene	79-01-6		0.453	1.00
Trichlorofluoromethane	75-69-4		0.484	1.00
1,2,3-Trichloropropane	96-18-4		0.628	5.00
Vinyl Acetate	108-05-4		0.716	5.00
Vinyl chloride	75-01-4		0.540	1.00
m,p-Xylene	1330-20-7		0.903	2.00
o-Xylene			0.449	1.00
Xylenes, total	1330-20-7		1.35	2.00

*Pre construction levels will be used in evaluating the post-construction results

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Worksheet #15 – continued

UFP QAPP Worksheet #15-12
Matrix: Solid
Analytical Group: Pre- and Post-Construction Staging/Support Areas Pesticides/PCBs (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
Aldrin	309-00-2		0.0300	0.0500
alpha-BHC	319-84-6		0.0300	0.0500
beta-BHC	319-85-7		0.0300	0.0500
gamma-BHC (Lindane)	58-89-9		0.0300	0.0500
delta-BHC	319-86-8		0.0300	0.0500
Chlordane	57-74-9		0.0800	0.100
alpha-Chlordane	5103-71-9		0.0300	0.0500
gamma-Chlordane	12789-03-6		0.0300	0.0500
Dieldrin	60-57-1		0.0300	0.0500
4,4'-DDD	72-54-8		0.0400	0.0500
4,4'-DDE	72-55-9		0.0300	0.0500
4,4'-DDT	50-29-3		0.0100	0.0500
Endosulfan I	959-98-8		0.0300	0.0500
Endosulfan II	33213-65-9		0.0400	0.0500
Endosulfan sulfate	1031-07-8		0.0400	0.0500
Endrin	72-20-8		0.0200	0.0500
Endrin aldehyde	7421-93-4		0.0300	0.0500
Endrin ketone	53494-70-5		0.0400	0.0500
Heptachlor	76-44-8		0.0300	0.0500
Heptachlor epoxide	1024-57-3		0.0300	0.0500
Methoxychlor	72-43-5		0.0100	0.0500
Toxaphene	8001-35-2		0.290	0.300
PCB-1016	12674-11-2		0.0164	0.100
PCB-1221	11104-28-2		0.0423	0.100
PCB-1232	11141-16-5		0.00800	0.100
PCB-1242	53469-21-9		0.0220	0.100
PCB-1248	12672-29-6		0.0111	0.100
PCB-1254	11097-69-1		0.0228	0.100
PCB-1260	11096-82-5		0.0156	0.100

*Pre construction levels will be used in evaluating the post-construction results

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Worksheet #15 – continued

UFP QAPP Worksheet #15-13
Matrix: Solid
Analytical Group: Pre- and Post-Construction Staging/Support Areas Herbicides (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
2,4,5-T	93-76-5		2.3	8.3
2,4-D	94-75-7		5	7.3
2,4-DB	94-82-6		3	8.3
Dalapon	75-99-0		2.9	330
Dicamba	1918-22-9		1.9	8.3
Dichlorprop	120-36-5		1.1	8.3
Dinoseb	88-85-7		4.6	100
MCPA	94-74-6		190	2000
Mecoprop	93-65-2		170	2000
Pentachlorophenol	87-86-5		0.42	8.3
Silvex (2,4,5-TP)	93-72-1		10	8.3

*Pre construction levels will be used in evaluating the post-construction results

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Worksheet #15 – continued

U**FP QAPP Worksheet #15-14**
Matrix: Solid
Analytical Group: Borrow Source Metals (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit (mg/kg)	Test America MDL (mg/kg)	Test America RL (mg/kg)
Aluminum	7429-90-5	50,000	4.05	16.6
Antimony	7440-36-0	180	0.0492	0.200
Arsenic	7440-38-2	7.6	0.404	2.00
Barium	7440-39-3	37,000	0.144	3.33
Beryllium	7440-41-7	410	0.126	0.835
Cadmium	7440-43-9	550	0.173	5.00
Calcium	7440-70-2	-	5.26	166
Chromium	7440-47-3	790,000	0.148	6.65
Cobalt	7440-48-4	2,600	0.282	3.33
Copper	7440-50-8	20,000	0.0456	1.00
Iron	7439-89-6	160,000	5.50	16.6
Lead	7439-92-1	400	1.60	13.3
Magnesium	7439-95-4	1,000,000	1.66	166
Manganese	7439-96-5	25,000	0.0459	1.50
Mercury	7439-97-6	160	0.000300	0.00833
Nickel	7440-02-0	40,000	0.366	1.66
Potassium	7440-09-7	-	4.72	166
Selenium	7782-49-2	1,600	1.99	16.6
Silver	7440-22-4	2,500	0.0308	0.100
Sodium	7440-23-5	1,000,000	102	166
Thallium	7440-28-0	35	0.0412	0.200
Vanadium	7440-62-2	750	0.316	8.35
Zinc	7440-66-6	170,000	0.872	8.35

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Worksheet #15 – continued

U**FP QAPP Worksheet #15-15**
Matrix: Liquid
Analytical Group: Borrow Source (Rinseate) Metals (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (mg/L)	Test America MDL (mg/L)	Test America RL (mg/L)
Aluminum	7429-90-5		0.0210	0.100
Antimony	7440-36-0		0.000047	0.000200
Arsenic	7440-38-2		0.404	2.00
Barium	7440-39-3		0.00370	0.00100
Beryllium	7440-41-7		0.000390	0.000200
Cadmium	7440-43-9		0.00023	0.000200
Calcium	7440-70-2		0.113	1.00
Chromium	7440-47-3		0.00059	0.00100
Cobalt	7440-48-4		0.00044	0.000200
Copper	7440-50-8		0.0000462	0.00100
Iron	7439-89-6		0.00560	0.100
Lead	7439-92-1		0.00194	0.0800
Magnesium	7439-95-4		0.0465	1.00
Manganese	7439-96-5		0.000175	0.00100
Mercury	7439-97-6		0.0000449	0.000200
Nickel	7440-02-0		0.00079	0.00100
Potassium	7440-09-7		0.109	1.00
Selenium	7782-49-2		0.00307	0.00200
Silver	7440-22-4		0.0000101	0.0001
Sodium	7440-23-5		102	166
Thallium	7440-28-0		0.0000267	0.0002
Vanadium	7440-62-2		0.00054	0.0500
Zinc	7440-66-6		0.00315	0.0500

* Results will be evaluated against result reported for Borrow Source solid sample.

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Worksheet #15 – continued

UFP QAPP Worksheet #15-16
Matrix: Solid
Analytical Group: Borrow Source SVOC (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
Acenaphthene	83-32-9	4.1E+7	16.8	147
Acenaphthylene	208-96-8	1.6E+6	15.6	147
Aniline	62-53-3	3.3E+5	15.2	294
Anthracene	120-12-7	2.3E+8	50	495
Benzo (a) anthracene	56-55-3	20,000	7.89	147
Benzo (b) fluoranthene	205-99-2	20,000	17.5	147
Benzo (g,h,i) perylene	191-24-2	2.5E+6	12.3	147
Benzo (k) fluoranthene	207-08-9	2.0E+5	11.9	147
Benzo (a) pyrene	50-32-8	2,000	11.6	147
Benzyl alcohol	100-51-6	5.8E+6	19.9	294
Bis(2-chloroethyl)ether	111-44-4	13,000	30.7	147
Bis(2-ethylhexyl) phthalate	117-81-7	2.8E+6	84.5	147
Butyl benzyl phthalate	85-68-7	3.1E+5	37.6	147
Carbazole	86-74-8	5.3E+5	27.9	147
4-Chloro-3-methylphenol	59-50-7	4.5E+6	14.9	294
2-Chloronaphthalene	91-58-7	5.6E+7	22	147
2-Chlorophenol	95-57-8	1.4E+6	26.7	294
Chrysene	218-01-9	2.0E+6	8.97	147
Dibenzofuran	132-64-9	-	27	147
Dibenz(a,h)anthracene	53-70-3	2,000	12	147
1,2-Dichlorobenzene	95-50-1	2.1E+5	3	147
1,3-Dichlorobenzene	541-73-1	1.7E+5	24	147
1,4-Dichlorobenzene	106-46-7	4.0E+5	29.5	147
Di-n-butyl phthalate	84-74-2	-	62.6	147
3,3'-Dichlorobenzidine	91-94-1	6,600	102	1470
2,4-Dichlorophenol	120-83-2	6.6E+5	23.5	294
Diethyl phthalate	84-66-2	7.4E+5	31.9	147
2,4-Dimethylphenol	105-67-9	1.1E+7	21	147
Fluoranthene	206-44-0	4.6E+7	12.2	147
Fluorene	86-73-7	2.7E+7	17.2	147
Hexachlorobenzene	118-74-1	8,900	25.3	147
Hexachlorobutadiene	87-68-3	1.0E+5	15.7	147
Hexachlorocyclopentadiene	77-47-4	7.2E+5	19.1	588
Hexachloroethane	67-72-1	2.3E+5	24.2	147
Indeno (1,2,3-cd) pyrene	193-39-5	20,000	11.8	147
Isophorone	78-59-1	2.4E+6	28.7	147
2-Methylnaphthalene	91-57-6	8.1E+6	19.9	147
Naphthalene	91-20-3	1.6E+7	15.5	147
Nitrobenzene	98-95-3	1.0E+5	29.8	147
2-Nitrophenol	88-75-5	6.3E+5	31	294
N-Nitrosodiphenylamine	86-30-6	1.7E+6	27.1	147
N-Nitrosodi-n-propylamine	621-64-7	1,200	29.7	147

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Worksheet #15 – continued

Worksheet 15-16 – Borrow Source SVOCs

Analyte	CAS Number	Project Action Limit (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
Pentachlorophenol	87-86-5	90,000	27.8	294
Phenanthrene	85-01-8	1.6E+6	12.2	147
Phenol	108-95-2	1.2E+7	33.7	294
Pyrene	129-00-0	2.9E+7	15.5	147
Pyridine	110-86-1	37,000	58.3	147
1,2,4-Trichlorobenzene	120-82-1	-	16.9	147
2,4,5-Trichlorophenol	95-95-4	2.3E+7	28.2	294
2,4,6-Trichlorophenol	88-06-2	7.1E+5	20	294

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Worksheet #15 – continued

U**FP QAPP Worksheet #15-17**
Matrix: Liquid
Analytical Group: Borrow Source (Rinseate) SVOC (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (ug/L)	Test America MDL (ug/L)	Test America RL (ug/L)
Acenaphthene	83-32-9		0.232	5.00
Acenaphthylene	208-96-8		0.266	5.00
Aniline	62-53-3		0.496	10.00
Anthracene	120-12-7		0.286	5.00
Benzo (a) anthracene	56-55-3		0.333	5.00
Benzo (b) fluoranthene	205-99-2		0.316	5.00
Benzo (g,h,i) perylene	191-24-2		0.202	5.00
Benzo (k) fluoranthene	207-08-9		0.314	5.00
Benzo (a) pyrene	50-32-8		0.318	5.00
Benzyl alcohol	100-51-6		0.486	10.00
Bis(2-chloroethyl)ether	111-44-4		0.570	5.00
Bis(2-ethylhexyl) phthalate	117-81-7		0.156	5.00
Butyl benzyl phthalate	85-68-7		0.618	5.00
Carbazole	86-74-8		0.203	5.00
4-Chloro-3-methylphenol	59-50-7		0.530	5.00
2-Chloronaphthalene	91-58-7		0.952	5.00
2-Chlorophenol	95-57-8		0.566	10.00
Chrysene	218-01-9		0.373	5.00
Dibenzofuran	132-64-9		0.197	5.00
Dibenz(a,h)anthracene	53-70-3		0.191	5.00
1,2-Dichlorobenzene	95-50-1		0.348	5.00
1,3-Dichlorobenzene	541-73-1		0.337	5.00
1,4-Dichlorobenzene	106-46-7		0.523	5.00
Di-n-butyl phthalate	84-74-2		0.779	5.00
3,3'-Dichlorobenzidine	91-94-1		0.426	50.00
2,4-Dichlorophenol	120-83-2		0.484	10.00
Diethyl phthalate	84-66-2		0.533	5.00
2,4-Dimethylphenol	105-67-9		0.562	10.0
Dimethyl phthalate			0.534	5.00
2,4-Dinitrotoluene	121-14-2		0.424	5.00
Fluoranthene	206-44-0		0.238	5.00
Fluorene	86-73-7		0.267	5.00
Hexachlorobenzene	118-74-1		0.321	5.00
Hexachlorobutadiene	87-68-3		0.694	5.00
Hexachlorocyclopentadiene	77-47-4		10	20.00
Hexachloroethane	67-72-1		0.464	5.00
Indeno (1,2,3-cd) pyrene	193-39-5		0.216	5.00
Isophorone	78-59-1		0.596	5.00
2-Methylnaphthalene	91-57-6		0.275	5.00
Naphthalene	91-20-3		0.369	5.00
Nitrobenzene	98-95-3		0.926	5.00
2-Nitrophenol	88-75-5		0.501	10.00
N-Nitrosodiphenylamine	86-30-6		0.307	5.00

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Worksheet #15 – continued

Worksheet 15-17 – Borrow Source SVOCs

Analyte	CAS Number	Project Action Limit* (ug/L)	Test America MDL (ug/L)	Test America RL (ug/L)
N-Nitrosodi-n-propylamine	621-64-7		0.553	5.00
Pentachlorophenol	87-86-5		0.417	10.0
Phenanthrene	85-01-8		0.203	5.00
Phenol	108-95-2		0.525	10.0
Pyrene	129-00-0		0.255	5.00
Pyridine	110-86-1		0.455	5.00
1,2,4-Trichlorobenzene	120-82-1		0.619	5.00
2,4,5-Trichlorophenol	95-95-4		0.626	10.0
2,4,6-Trichlorophenol	88-06-2		0.886	10.0

* Results will be evaluated against result reported for Borrow Source solid sample.

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Worksheet #15 – continued

UFP QAPP Worksheet #15-18
Matrix: Solid
Analytical Group: Borrow Source (solid) VOCs (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
Acetone	67-64-1	2.3E+7	9.03	100
Acrolein	107-02-8	3.6E+6	12.9	50.0
Acrylonitrile	107-13-1	16,000	1.77	5.00
Allyl chloride	107-05-1	-	1.51	5.00
Benzene	71-43-2	1.8E+5	1.32	5.00
Bromobenzene	108-86-1	5.4E+5	1.34	5.00
Bromochloromethane	74-97-5	-	1.41	5.00
Bromodichloromethane	75-27-4	1.1E+5	1.52	5.00
Bromoform	75-25-2	8.2E+5	1.57	5.00
Bromomethane (Methyl bromide)	74-83-9	3.2E+5	1.29	10.0
2-Butanone (MEK)	78-93-3	2.7E+7	3.98	50.0
tert-Butylbenzene	98-06-6	2.5E+6	1.22	5.00
sec-Butylbenzene	135-98-8	2.5E+6	1.75	5.00
n-Butylbenzene	104-51-8	2.5E+6	1.34	5.00
Carbon disulfide	75-15-0	2.8E+5	1.28	5.00
Carbon tetrachloride	56-23-5	96,000	1.39	5.00
Chlorobenzene	108-90-7	2.6E+5	1.31	5.00
Chloroethane	75-00-3	9.5E+5	1.41	5.00
2-Chloroethylvinyl ether	110-75-8	-	2.81	5.00
Chloroform	67-66-3	1.2E+6	1.18	5.00
Chloromethane (Methyl chloride)	74-87-3	1.1E+6	1.28	10.0
Chloroprene	126-99-8	-	1.33	5.00
4-Chlorotoluene	106-43-4	-	1.12	5.00
2-Chlorotoluene	95-49-8	5.0E+5	1.15	5.00
Cyclohexane	110-82-7	2.2E+8	3.32	5.00
Dibromochloromethane	124-48-1	1.1E+5	1.49	5.00
1,2-Dibromo-3-chloropropane	96-12-8	-	1.76	5.00
1,2-Dibromoethane (EDB)	106-93-4	-	1.43	5.00
Dibromomethane	74-95-3	2.0E+6	1.64	5.00
trans-1,4-Dichloro-2-butene	110-57-6	-	2.02	5.00
1,2-Dichlorobenzene	95-50-1	2.1E+5	1.91	5.00
1,4-Dichlorobenzene	106-46-7	4.0E+5	1.27	5.00
1,3-Dichlorobenzene	541-73-1	1.7E+5	1.90	5.00
Dichlorodifluoromethane	75-71-8	1.0E+6	1.10	5.00
1,1-Dichloroethane	75-34-3	8.9E+5	1.09	5.00
1,2-Dichloroethane	107-06-2	91,000	1.40	5.00
cis-1,2-Dichloroethene	156-59-2	6.4E+5	1.55	5.00
trans-1,2-Dichloroethene	156-60-5	1.4E+6	1.34	5.00
1,2-Dichloroethene (total)	540-59-0	-	1.55	5.00
1,1-Dichloroethene	75-35-4	2.0E+5	1.55	5.00
1,3-Dichloropropane	142-28-9	-	1.46	5.00
2,2-Dichloropropane	594-20-7	-	1.36	5.00
1,2-Dichloropropane	78-87-5	1.4E+5	1.35	5.00
1,1-Dichloropropene	563-58-6	-	1.35	5.00

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Worksheet #15 – continued

Worksheet 15-18 – Borrow Source VOCs

Analyte	CAS Number	Project Action Limit (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
cis-1,3-Dichloropropene	10061-01-5	-	1.31	5.00
1,3-Dichloropropene (total)	NA	-	1.37	5.00
trans-1,3-Dichloropropene	10061-02-6	-	1.37	5.00
Diethyl ether	60-29-7	7.4E+6	1.56	5.00
Ethyl acetate	141-78-6	7.5E+6	3.75	50.0
Ethylbenzene	100-41-4	1.4E+5	1.37	5.00
Ethyl methacrylate	97-63-2	-	1.65	5.00
Hexachlorobutadiene	87-68-3	1.0E+5	1.63	5.00
n-Hexane	110-54-3	44,000	8.06	20.0
2-Hexanone	591-78-6	2.5E+6	4.64	50.0
Iodomethane	74-88-4	-	1.18	5.00
Isopropylbenzene (Cumene)	98-82-8	3.9E+5	1.31	5.00
p-Isopropyltoluene	99-87-6	-	1.26	5.00
Methacrylonitrile	126-98-7	-	1.93	5.00
Methyl tert-butyl ether	1634-04-4	1.5E+6	2.31	5.00
Methylene chloride	75-09-2	1.3E+6	4.94	10.0
Methyl methacrylate	80-62-6	-	1.60	5.00
2-Methylnaphthalene	91-57-6	8.1E+6	1.82	5.00
4-Methyl-2-pentanone (MIBK)	108-10-1	2.7E+6	4.77	50.0
Naphthalene	91-20-3	1.6E+7	2.24	5.00
2-Nitropropane	79-46-9	-	1.48	10.0
Propionitrile	107-12-0	-	7.54	50.0
n-Propylbenzene	103-65-1	2.5E+6	1.69	5.00
Pentachloroethane	76-01-7	-	1.22	5.00
Styrene	100-42-5	4.0E+5	1.48	5.00
1,1,1,2-Tetrachloroethane	630-20-6	4.4E+5	1.27	5.00
1,1,2,2-Tetrachloroethane	79-34-5	53,000	1.61	5.00
Tetrachloroethene	127-18-4	88,000	1.44	5.00
Toluene	108-88-3	2.5E+5	1.35	5.00
1,2,3-Trichlorobenzene	87-61-6	-	3.11	5.00
1,2,4-Trichlorobenzene	120-82-1	9.9E+5	2.37	5.00
1,1,1-Trichloroethane	71-55-6	4.6E+5	1.37	5.00
1,1,2-Trichloroethane	79-00-5	1.8E+5	1.47	5.00
Trichloroethene	79-01-6	5.0E+5	1.29	5.00
Trichlorofluoromethane	75-69-4	5.6E+5	1.43	5.00
1,2,3-Trichloropropane	96-18-4	8.3E+5	1.70	5.00
1,1,2-Trichlorotrifluoroethane	76-13-1	-	1.39	5.00
1,2,4-Trimethylbenzene	95-63-6	1.1E+5	1.71	5.00
1,3,5-Trimethylbenzene	108-67-8	94,000	1.23	5.00
Vinyl Acetate	108-05-4	2.4E+6	1.40	5.00
Vinyl chloride	75-01-4	3,8000	1.52	5.00
m,p-Xylene	1330-20-7	-	2.36	5.00
o-Xylene	95-47-6	-	1.29	5.00
Xylenes, total	1330-20-7	1.5E+8	2.36	5.00

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Worksheet #15 – continued

UFP QAPP Worksheet #15-19
Matrix: Liquid
Analytical Group: Borrow Source (trip blank/rinseate) VOCs (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (ug/L)	Test America MDL (ug/L)	Test America RL (ug/L)
Acetone	67-64-1		6.25	20.0
Acrolein	107-02-8		22.8	50.0
Acrylonitrile	107-13-1		1.72	5.00
Allyl chloride	107-05-1		0.438	5.00
Benzene	71-43-2		0.456	1.00
Bromobenzene	108-86-1		0.570	1.00
Bromochloromethane	74-97-5		0.472	1.00
Bromodichloromethane	75-27-4		0.402	1.00
Bromoform	75-25-2		0.411	1.00
Bromomethane (Methyl bromide)	74-83-9		0.645	1.00
2-Butanone (MEK)	78-93-3		2.08	10.0
tert-Butylbenzene	98-06-6		0.459	1.00
sec-Butylbenzene	135-98-8		0.366	1.00
n-Butylbenzene	104-51-8		0.355	1.00
Carbon disulfide	75-15-0		0.446	1.00
Carbon tetrachloride	56-23-5		0.439	1.00
Chlorobenzene	108-90-7		0.450	1.00
Chloroethane	75-00-3		0.446	5.00
2-Chloroethylvinyl ether	110-75-8		0.481	5.00
Chloroform	67-66-3		1.18	1.00
Chloromethane (Methyl chloride)	74-87-3		0.490	5.00
Chloroprene	126-99-8		0.405	5.00
4-Chlorotoluene	106-43-4		0.418	1.00
2-Chlorotoluene	95-49-8		0.555	1.00
Cyclohexane	110-82-7		0.457	5.00
Dibromochloromethane	124-48-1		1.49	1.00
1,2-Dibromo-3-chloropropane	96-12-8		1.47	5.00
1,2-Dibromoethane (EDB)	106-93-4		0.444	5.00
Dibromomethane	74-95-3		0.488	1.00
trans-1,4-Dichloro-2-butene	110-57-6		2.02	5.00
1,2-Dichlorobenzene	95-50-1		0.503	1.00
1,4-Dichlorobenzene	106-46-7		0.435	1.00
1,3-Dichlorobenzene	541-73-1		0.424	1.00
Dichlorodifluoromethane	75-71-8		0.800	1.00
1,1-Dichloroethane	75-34-3		0.468	1.00
1,2-Dichloroethane	107-06-2		0.534	1.00
cis-1,2-Dichloroethene	156-59-2		0.453	1.00
trans-1,2-Dichloroethene	156-60-5		0.449	1.00
1,2-Dichloroethene (total)	540-59-0		1.55	2.00
1,1-Dichloroethene	75-35-4		0.451	1.00
1,3-Dichloropropane	142-28-9		0.454	1.00
2,2-Dichloropropane	594-20-7		0.391	1.00
1,2-Dichloropropane	78-87-5		0.467	1.00
1,1-Dichloropropene	563-58-6		0.464	1.00

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Worksheet #15 – continued

Worksheet 15-19 – Borrow Source (trip blank/rinseate) VOCs

Analyte	CAS Number	Project Action Limit* (ug/L)	Test America MDL (ug/L)	Test America RL (ug/L)
cis-1,3-Dichloropropene	10061-01-5		0.467	1.00
1,3-Dichloropropene (total)	NA		1.37	2.00
trans-1,3-Dichloropropene	10061-02-6		0.638	1.00
Diethyl ether	60-29-7		1.58	2.00
Ethyl acetate	141-78-6		3.75	5.00
Ethylbenzene	100-41-4		0.419	1.00
Ethyl methacrylate	97-63-2		0.525	5.00
Hexachlorobutadiene	87-68-3		0.938	5.00
n-Hexane	110-54-3		1.56	5.00
2-Hexanone	591-78-6		2.85	10.0
Iodomethane	74-88-4		0.503	5.00
Isopropylbenzene (Cumene)	98-82-8		0.397	1.00
p-Isopropyltoluene	99-87-6		1.26	1.00
Methacrylonitrile	126-98-7		0.572	5.00
Methyl tert-butyl ether	1634-04-4		0.518	1.00
Methylene chloride	75-09-2		0.528	2.00
Methyl methacrylate	80-62-6		0.534	5.00
2-Methylnaphthalene	91-57-6		1.82	5.00
4-Methyl-2-pentanone (MIBK)	108-10-1		1.53	10.0
Naphthalene	91-20-3		2.00	5.00
2-Nitropropane	79-46-9		1.48	5.00
Propionitrile	107-12-0		4.10	50.0
n-Propylbenzene	103-65-1		0.519	1.00
Pentachloroethane	76-01-7		0.439	1.00
Styrene	100-42-5		0.485	1.00
1,1,1,2-Tetrachloroethane	630-20-6		0.458	1.00
1,1,2,2-Tetrachloroethane	79-34-5		0.953	1.00
Tetrachloroethene	127-18-4		0.450	1.00
Toluene	108-88-3		0.522	1.00
1,2,3-Trichlorobenzene	87-61-6		3.11	5.00
1,2,4-Trichlorobenzene	120-82-1		1.31	5.00
1,1,1-Trichloroethane	71-55-6		0.426	1.00
1,1,2-Trichloroethane	79-00-5		0.643	1.00
Trichloroethene	79-01-6		0.453	1.00
Trichlorofluoromethane	75-69-4		0.484	1.00
1,2,3-Trichloropropane	96-18-4		0.628	5.00
1,1,2-Trichlorotrifluoroethane	76-13-1		0.837	1.00
1,2,4-Trimethylbenzene	95-63-6		0.335	1.00
1,3,5-Trimethylbenzene	108-67-8		0.388	1.00
Vinyl Acetate	108-05-4		0.716	5.00
Vinyl chloride	75-01-4		0.540	1.00
m,p-Xylene	1330-20-7		0.903	2.00
o-Xylene	95-47-6		0.449	1.00
Xylenes, total	1330-20-7		1.35	2.00

* Results will be evaluated against result reported for Borrow Source solid sample.

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Worksheet #15 – continued

UFP QAPP Worksheet #15-20
Matrix: Solid
Analytical Group: Borrow Source Pesticides/PCBs (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
Aldrin	309-00-2	1,000	0.0300	0.0500
alpha-BHC	319-84-6	-	0.0300	0.0500
beta-BHC	319-85-7	-	0.0300	0.0500
gamma-BHC (Lindane)	58-89-9	8,300	0.0300	0.0500
delta-BHC	319-86-8	-	0.0300	0.0500
Chlordane	57-74-9	31,000	0.0800	0.100
alpha-Chlordane	5103-71-9	-	0.0300	0.0500
gamma-Chlordane	12789-03-6	-	0.0300	0.0500
Dieldrin	60-57-1	1,00	0.0300	0.0500
4,4'-DDD	72-54-8	95,000	0.0400	0.0500
4,4'-DDE	72-55-9	45,000	0.0300	0.0500
4,4'-DDT	50-29-3	57,000	0.0100	0.0500
Endosulfan I	959-98-8	-	0.0300	0.0500
Endosulfan II	33213-65-9	-	0.0400	0.0500
Endosulfan sulfate	1031-07-8	-	0.0400	0.0500
Endrin	72-20-8	65,000	0.0200	0.0500
Endrin aldehyde	7421-93-4	-	0.0300	0.0500
Endrin ketone	53494-70-5	-	0.0400	0.0500
Heptachlor	76-44-8	5,000	0.0300	0.0500
Heptachlor epoxide	1024-57-3	3,100	0.0300	0.0500
Methoxychlor	72-43-5	1.9E+6	0.0100	0.0500
Toxaphene	8001-35-2	20,000	0.290	0.300
PCB-1016	12674-11-2		0.0164	0.100
PCB-1221	11104-28-2		0.0423	0.100
PCB-1232	11141-16-5		0.00800	0.100
PCB-1242	53469-21-9		0.0220	0.100
PCB-1248	12672-29-6		0.0111	0.100
PCB-1254	11097-69-1		0.0228	0.100
PCB-1260	11096-82-5		0.0156	0.100

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Worksheet #15 – continued

UFP QAPP Worksheet #15-21
Matrix: Liquid
Analytical Group: Borrow Source (Rinseate) Pesticides/PCBs (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (ug/L)	Test America MDL (ug/L)	Test America RL (ug/L)
Aldrin	309-00-2		0.0260	0.1000
alpha-BHC	319-84-6		0.0310	0.1000
beta-BHC	319-85-7		0.0300	0.1000
gamma-BHC (Lindane)	58-89-9		0.0380	0.1000
delta-BHC	319-86-8		0.0300	0.1000
Chlordane	57-74-9		0.130	0.2000
alpha-Chlordane	5103-71-9		0.0280	0.1000
gamma-Chlordane	12789-03-6		0.0290	0.1000
Dieldrin	60-57-1		0.0290	0.1000
4,4'-DDD	72-54-8		0.0280	0.1000
4,4'-DDE	72-55-9		0.0280	0.1000
4,4'-DDT	50-29-3		0.0440	0.1000
Endosulfan I	959-98-8		0.0290	0.1000
Endosulfan II	33213-65-9		0.0290	0.1000
Endosulfan sulfate	1031-07-8		0.0370	0.1000
Endrin	72-20-8		0.0320	0.1000
Endrin aldehyde	7421-93-4		0.0300	0.1000
Endrin ketone	53494-70-5		0.300	1.000
Heptachlor	76-44-8		0.0560	0.1000
Heptachlor epoxide	1024-57-3		0.0400	0.1000
Methoxychlor	72-43-5		0.0470	0.1000
Toxaphene	8001-35-2		0.170	0.200
PCB-1016	12674-11-2		0.0458	0.200
PCB-1221	11104-28-2		0.0458	0.200
PCB-1232	11141-16-5		0.0458	0.200
PCB-1242	53469-21-9		0.0458	0.200
PCB-1248	12672-29-6		0.0614	0.200
PCB-1254	11097-69-1		0.0614	0.200
PCB-1260	11096-82-5		0.0614	0.200

* Results will be evaluated against result reported for Borrow Source solid sample.

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Worksheet #15 – continued

UFP QAPP Worksheet #15-22
Matrix: Solid
Analytical Group: Borrow Source Herbicides (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
2,4,5-T	93-76-5	-	2.3	8.3
2,4-D	94-75-7	-	5	7.3
2,4-DB	94-82-6	-	3	8.3
Dalapon	75-99-0	1.9E+7	2.9	330
Dicamba	1918-22-9	3.4E+6	1.9	8.3
Dichlorprop	120-36-5	-	1.1	8.3
Dinoseb	88-85-7	66,000	4.6	100
MCPA	94-74-6	-	190	2000
Mecoprop	93-65-2	-	170	2000
Pentachlorophenol	87-86-5	90,000	0.42	8.3
Silvex (2,4,5-TP)	93-72-1	1.7E+6	10	8.3

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Worksheet #15 – continued

UFP QAPP Worksheet #15-23
Matrix: Liquid
Analytical Group: Borrow Source (Rinseate) Herbicides (SW846)
Concentration Level: Medium

Analyte	CAS Number	Project Action Limit* (ug/L)	Test America MDL (ug/L)	Test America RL (ug/L)
2,4,5-T	93-76-5		0.300	1.00
2,4-D	94-75-7		0.410	4.00
2,4-DB	94-82-6		0.690	4.00
Dalapon	75-99-0		0.170	2.00
Dicamba	1918-22-9		0.520	2.00
Dichlorprop	120-36-5		0.860	4.00
Dinoseb	88-85-7		0.087	0.60
MCPA	94-74-6		390	400
Mecoprop	93-65-2		400	400
Pentachlorophenol	87-86-5		0.024	0.10
Silvex (2,4,5-TP)	93-72-1		0.200	1.00

* Results will be evaluated against result reported for Borrow Source solid sample.

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QAPP Worksheet #16 Project Schedule/Timeline Table

Activities	Organization	Dates (Month Day, Year)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
QAPP Preparation (UFP format)	EQ	August 8, 2011	January 10, 2012	QAPP (UFP Format)	January 13, 2012
Investigative Sampling	EQ	August 30, 2011	September 15, 2013	Samples to laboratory	October 1, 2013
Laboratory Analysis	Test America Laboratory	Upon sample receipt by laboratory	2 weeks following sample receipt	Laboratory Data Report	October 15, 2013
Data Validation	EQ/WESTON	1 week following receipt of final data package	3 weeks following receipt of final data package	Data Validation Report	November 15, 2013
Final Project Report	EQ	August 15, 2014	December 15, 2014	Final Report	December 30, 2014

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QAPP Worksheet #17 Sampling Design and Rationale

Describe and provide a rationale for choosing the sampling approach (*e.g.*, grid system, biased statistical approach):

- Pre-removal PCB soil and sediment concentrations in removal areas will be a biased approach to ensure data is obtained for grids that EPA currently does not have PCB sample results.
- Sampling for pre- and post-construction conditions of surface soils in support areas will be accomplished using a grid system. Within each grid the 6 point composite sample locations will be selected randomly. Each sample point location for pre-construction conditional will be located using GPS. Post-construction sampling will be accomplished by sampling at these same locations.
- Waste characterization of sediments will be accomplished by compositing representative material for each waste stream that requires disposal.
- Sampling for borrow source (backfill) material will be performed by taking one six point composite for every 5000 cubic yards of each type of material (i.e., soil, sand, river rock) at each source location.
- Surface soil samples in Upjohn Park will be performed by applying a biased approach. Each sample will be a grab sample taken at locations where sediments are expected to be deposited during flooding events.
- Wastewater treatment effluent monitoring will be targeted at specific locations to monitor the effectiveness of the wastewater treatment system as well as compliance with applicable discharge permits.
- Personnel and area monitoring will be performed on a biased approach, targeting individuals and areas most likely to be impacted by work activities.
- Surface water quality monitoring in the stream will be performed at targeted locations to ensure control measures implemented are effective in containing contaminated sediments while removal activities are under way.
- Post-excavation soil and sediment conditions (confirmation sampling) will be performed within the pre-established removal grids. One composite sample will be taken for each grid. Six locations within each grid will be randomly selected.

All applicable QC samples (duplicates, blanks, and matrix spikes) will also be collected.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations) [Refer to Worksheet #18 for details]:

The number of samples per matrix and location are presented in Table 11a. All applicable QC samples (duplicates, blanks, and matrix spikes) will also be collected.

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QAPP Worksheet #18 Sampling Locations and Methods/SOP Requirements Table

Sampling Location/ ID Number[1]	Matrix	Depth	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)[2]	Sampling SOP Reference	Rationale for Sampling Location
See Figures 3-9 for locations See Table 18a for nomenclature	sediment and/or soil	See Table 10a	PCBs	High/Medium	113 samples 12 FDs	SP-Soil-1	See Worksheet #17
See Figure 2 for Removal Areas See Table 18a for nomenclature	sediment	See Table 10a	Waste Characterization	High	TBD No FDs	SP-Watr-7	See Worksheet #17
Upjohn Park/ UJP-SS-Date-Sample Number	surface soils	0-6 in bgs	PCBs	Low	12-20 2 FDs	SP-Soil-4	See Worksheet #17
Staging/Support Areas/ PREC(or PSTC)-Support Area Name-Removal Area-Sample Number	surface soils	0-6 in bgs	VOCs, SVOCs, Metals, PCBs	Medium	1 sample/2,500 sf for PCBs; 1 sample/10,000 sf for all other parameters 1 FD/10 samples	SP-Soil-4	See Worksheet #17
Borrow Source/ BS-Vendor-Material-Date-Sample Number	Solid (soils, sand, rock)	NA	VOCs, SVOCs, Metals, PCBs	Low	1 sample/5000 cy	NA	See Worksheet #17
Turbidity Monitoring Stations/ Area-Location(US or DS200 or DS300)-SW-Date-Time	Surface Water	Mid-Depth	Turbidity	Medium	1 measurement every 30 minutes during removal activities	SP-Watr-7	See Worksheet #17
Turbidity Monitoring Stations/ Area-Location(US or DS200 or DS300)-SW-Date-Time	Surface Water	Mid-Depth	PCBs, TSS – weekly Phosphorus - monthly	Low	1 sample/week during removal activities	SP-Watr-7	See Worksheet #17
Personnel Workers/ Task-Date	air	NA	PCBs	Low	TBD	SP-Air-9	See Worksheet #17

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Worksheet #18 – continued

Sampling Location/ ID Number[1]	Matrix	Depth	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)[2]	Sampling SOP Reference	Rationale for Sampling Location
Work Area/ PRA(or SA)- Removal Area	air	NA	PCBs, Particulates	Low	TBD	SP-Air-8 SP-Air-9	See Worksheet #17
Wastewater Treatment/ WWINF(or MID, or EFF)-Date	wastewater	NA	PCBs, TSS – weekly Phosphorus - monthly	Low	1 sample/week during removal activities	NA	See Worksheet #17
Removal Grids/ CSD(or NSD)- Removal Area-Grid ID	sediment	0-6 in	PCBs	Low	72 composite samples 8 FD of composites 48 Grab samples	SP-Soil-1	See Worksheet #17

Notes:
[1] See Table 18a for explanation on sample nomenclature
[2] MS/MSD and field duplicate samples will be collected at a frequency of 1 for every 20 samples

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Worksheet #18 – continued

TABLE 18a. SAMPLE NOMENCLATURE

Sampling Task	Sample ID	Matrix ID	Example	Explanation
Targeted Grid Sampling/Pre-Removal Data Gaps	PRSD-Removal Area-Grid ID-Core number (depth interval)	SD	PRSD-SA5-A6-1 (0-12”)	*Pre-removal sediment sampling from Removal Area 5A, grid A6, core number one at 0-12”*
Waste Characterization	WCSD-Removal Area-A or B	SD	WCSD-SA5A-A	*Waste characterization composite sample taken from Removal Area 5A, TSCA sediment*
Pre- & Post-Construction/ Staging or Support Areas	PREC(or PSTC)-Support Area name-Removal Area sample number	SO	PSTC-Staging Pad-SA7-1	*Post-Construction Sample #1 taken from Staging Pad at Removal Area 7*
Upjohn Park Surface Soils	UJP-SS- Date-Sample number	SO	UJS-SS-093111-10	*10th Surface Soil Sample taken at Upjohn Park on 9/31/11*
Borrow Source Material	BS-Vendor-Material-Date-sample number	SO	BS-Joe’s Fill-sand-100511-1	*First sample taken of Borrow Source sample of sand material taken from vendor ‘Joe’s Fill’ on 10/5/11*
Surface Water Quality Monitoring	Area-Location (US or DS200 or DS300)-SW-Date	SW	SA3A-DS300-SW-101511	*Surface water sample taken on 10/15/11at turbidity monitoring station located 300 ft downstream of Removal Area SA3A*
Personnel Workers	Task-Date	AR	Excavator-101011	*Personnel sample taken of worker on excavator on 10/10/11*
Area Monitoring	PRA(or SA)-Removal Area-Date-#	AR	PSA-SA7-092911-1	*First perimeter air sample taken in the support area for Removal Area 7 on 9/29/11*
Waste Water Treatment Sampling	WWINF(or MID, EFF)-Date	WW	WWINF-093011	*Wastewater sample taken at influent on 9/30/11*
Confirmation Sediment Sampling	CSD-Removal Area-Grid ID	SD	CSD-SA5-A7	*Confirmation sediment sample taken from Removal Area 5, Grid A7*
Node Sediment Sampling	NSD-Removal Area-Grid ID-#	SD	NSD-SA6-13-1	*Node confirmation sediment sample taken from Removal Area 6, Grid 13, sample number 1*

Notes:
1. ID – identification, SD – sediment, WC – waste characterization, SO – soil/solid, SW – surface water, AR – air, WW – waste water, BS – borrow source
2. PREC – pre-construction, PSTC – post-construction, UP – 200 ft upstream of removal area, DS200 – 200 ft downstream of removal area, DS300 – 300 ft downstream of removal area
3. INF – influent, MID – between GAC, EFF – effluent
4. All dates are recorded as MMDDYY

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QAPP Worksheet #19 Analytical SOP Requirements Table

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/ SOP Reference[1]	Containers (number, size, and type)	Preservation Requirements	Maximum Holding Time (preparation/analysis)
Sediment /Soil	PCBs	Low	SW8082/ DT-ORG-017.1	1 8-oz glass jar	4ºC	14 days for extraction, 40 days for analysis
Sediment	TCLP VOCs	High	SW1311/8260 DT-ORG-003.2/DT-ORG-007.1	4-oz Gl WM	4°C	14 days for TCLP extraction, 14 days for analysis
Sediment	TCLP SVOCs	High	SW1311/8270/ DT-ORG-003.2/DT-ORG-008.1	8-oz Gl WM[2]	4°C	14 days for TCLP extraction, 7 days for preparative extraction, 40 days for analysis
Sediment	TCLP Pesticides	High	SW1311/8081/ DT-ORG-003.2/DT-ORG-015.1	8-oz Gl WM[2]	4°C	14 days for TCLP extraction, 7 days for preparative extraction, 40 days for analysis
Sediment	TCLP Herbicides	High	SW1311/8151/ DT-ORG-003.2/SOP Herbicides SAV	8-oz Gl WM[2]	4°C	14 days for TCLP extraction, 7 days for preparative extraction, 40 days for analysis
Sediment	TCLP 8 RCRA Metals	High	SW1311/6010, 7470/ DT-ORG-003.2/DT-MET-016.0. DT-MET-018.2	8-oz Gl WM[2]	4°C	28 days for Hg, 6 months for all other metals for TCLP extraction, 28 days for Hg, 6 months for all other metals for analysis
Sediment	PCBs	High	SW8082/ DT-ORG-017.1	4 oz, Gl[2]	4°C	14 days for analysis
Sediment	Total Cyanide	High	SW9012/DT-WET-060.1	4 oz, Gl[2]	4°C	14 days for analysis
Sediment	Total Sulfide	High	SW9034/SOP Sulfide SAV	4 oz, Gl[2]	4°C	7 days for analysis
Sediment	Flashpoint	High	SW1010/DT-WET-064.1	4 oz, Gl[2]	4°C	None
Sediment	pH	High	SW9045/DT-WET-019.1	4 oz, Gl[2]	4°C	Immediately
Solids (soil, sand, rock)	TCL VOCs	Low	SW8260/ DT-ORG-007.1	4-oz Gl WM	4°C	14 days for analysis
Solids (soil, sand, rock)	TCL SVOCs	Low	SW8270/ DT-ORG-008.1	8-oz Gl WM[3]	4°C	14 days for extraction, 40 days for analysis
Solids (soil, sand, rock)	TCL Pesticides	Low	SW8081//DT-ORG-015.1	8-oz Gl WM[3]	4°C	14 days for extraction, 40 days for analysis
Solids (soil, sand, rock)	TCL Herbicides	Low	SW8151/ SOP Herbicides SAV	8-oz Gl WM[3]	4°C	14 days for extraction, 40 days for analysis

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Worksheet #19 – continued

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/ SOP Reference[1]	Containers (number, size, and type)	Preservation Requirements	Maximum Holding Time (preparation/analysis)
Solids (soil, sand, rock)	TAL Metals	Low	SW6010 or 6020 & 7471/DT-MET-016.0, DT-MET-024.0, DT-MET-018.2	8-oz Gl WM[3]	4°C	28 days for Hg and 6 months for all other metals
Solids (soil, sand, rock)	PCBs	Low	SW8082/ DT-ORG-017.1	4-oz Gl WM[3]	4°C	14 days for analysis
Water [4]	PCBs	Low	E608/ DT-ORG-002.1	1 L Gl Amber	4°C	7 days for extraction, 40 days for analysis
Water [4]	TSS	Low	SM2540D/DT-WET-029.1	500 ml, Pl	4°C	7 days for analysis
Water [4]	Phosphorus	Low	SM4500P/DT-WET-56.1	250 ml, Pl	H_2SO_4, 4°C	28 days for analysis
Air	PCBs	Low	NIOSH 5503	filter, sorbet tube[5]	4°C	2 months
Air	Total Particulates	Low	NIOSH 0500	PVC[6]	None	None

Notes:

1. SW – SW846 EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods; SM – Standard Methods for Analysis of Water and Wastewater; E – USEPA Clean Water Act Methods
2. One 32 oz jar may be submitted for TCLP (SVOCs, Pest, Metals), PCBs, Cyanide, Sulfide, flashpoint and pH
3. One 8 oz jar may be submitted for SVOCs, Pesticides, Metals, and PCBs
4. Includes surface water and wastewater
5. Glass fiber filter + solid sorbent (13-mm glass fiber + florisil, 100 mg/50 mg)
6. 37-mm, 5-µm PVC filter

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QAPP Worksheet #20 Field Quality Control Sample Summary Table

Matrix	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations	Frequency	No. of FDs	Inorganic No. of MS	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Total No. Samples to Lab
Sediment /Soil	PCBs	Medium	DT-ORG-017.1	113	Once	12	NA	0	0	0	125
Sediment	Waste Characterization	High	DT-ORG-003.2, DT-ORG-007.1, DT-ORG-008.1, DT-MET-016.0, DT-MET-018.2, DT-ORG-015.1, DOP Herbicides SAV, DT-WET-060.1, SOP Sulfide soil SAV, DT-WET-015.1, DT-WET-019.1, DT-WET-020.1	18-36	Once	0	0	0	0	0	TBD
Surface Soil	PCBs	Low	DT-ORG-017.1	12-20	Once	1/10	NA	0	0	0	14-22
Borrow Source[2]	VOCs, SVOCs, Pesticides/PCBs, Herbicides, Metals	Low	DT-ORG-007.1, DT-ORG-008.1, DT-MET-016.0, DT-MET-024.0 DT-MET-018.2, DT-ORG-017.1, DT-ORG-015.1, SOP Herbicides SAV	TBD	As Needed	1/10	1/20	1/10	1/10	0	TBD
Surface Soil	VOCs, SVOCs, Pesticides/PCBs, Herbicides, Metals	Medium	DT-ORG-007.1, DT-ORG-008.1, DT-MET-016.0, DT-MET-024.0 DT-MET-018.2, DT-ORG-017.1, DT-ORG-015.1, SOP Herbicides SAV	TBD	2 times (pre & post construction)	1/10	1/20	0	0	0	TBD

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Worksheet #20 – continued

Matrix	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations	Frequency	No. of FDs	Inorganic No. of MS	No. of Field Blanks	No. of Equip. Blanks	No. of PT Samples	Total No. Samples to Lab
Surface Water	Turbidity	Medium	FSP Section 2.3	TBD	Every thirty minutes during removal activities	0	NA	NA	NA	0	TBD
Surface Water	PCBs, TSS	Low	DT-WET-029.1, DT-ORG-002.1	TBD	Once per week during removal activities	1/10	0	0	0	0	TBD
Surface Water	Phosphorus	Low	DT-WET-023.1	TBD	Once per month during removal activities	1/10	0	0	0	0	TBD
Waste Water	PCBs, TSS	Low	DT-WET-029.1, DT-ORG-002.1	TBD	Once per week during wastewater treatment	1/10	0	0	0	0	TBD
Waste Water	Phosphorus	Low	DT-WET-023.1	TBD	Once per month during wastewater treatment	1/10	0	0	0	0	TBD
Sediment	PCBs	Low	DT-ORG-017.1	80	Once	8	0	0	0	0	88

Notes:

1. The reference letter or number is from the Analytical SOP References table (Worksheet #23).
2. Matrix will include soil, sand, and rock.

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QAPP Worksheet #21 Project Sampling SOP References Table

Reference Number	Title, Revision Date and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
SP-Air-8	Particulate Sampling – Real Time, Rev. 6	EQ	DataRam or similar type of direct read instrument	N	
SP-Air-9	Low-Volume Air Sampling, Rev. 6	EQ	Personnel Air Pumps	N	
SP-Othr-1	Sample Packaging, Shipment and Storage, Rev. 4	EQ	Sample Bottle(s)	N	
SP-Soil-1	Sediment Sampling and Handling Guidance, Rev. 4	EQ	Sediment Sampler	N	
SP-Soil-4	Surface Soil Sampling, Rev. 4	EQ	Scoop or Spoon	N	
SP-Watr-7	Surface Water Sampling, Rev 3	EQ	Sample Bottle(s)	N	

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

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
DataRam or similar type of direct read instrument	NA	Per Manufacturer Instructions						START or EQ Field Sampler	SP-Air-8
Personnel Air Pumps	Single point CalCheck calibration	Per Manufacturer Instructions			Prior to and Immediately after sampling	3 readings 1-3% difference	Repeat calibration, if still outside criteria replace pump	START or EQ Field Sampler	SP-Air-9
Turbidity Meter	NA	Per Manufacturer Instructions		Visually Inspect, ensure probe is clean	Daily Before Use	Auto-Cal program register complete	If fails to complete auto-cal program, follow manufacture recommendations	EQ Field Sampler	SP-Watr-1
Sediment Sampler	NA	Decontaminate and Store in Carrying Case	NA	Visually Inspect					
Sample bottle	NA	NA	NA	Check certification for each bottle lot for cleanliness.	Each bottle lot.	Accept only if each bottle lot is accompanied by certification for cleanliness.	Reject the bottles if not accompanied by cleanliness certification.	ERRS SMO	NA

Notes:
[1]The reference letter or number is from the Project Sampling SOP References table (Worksheet #21).
[2] SMO – Sample Management Office

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QAPP Worksheet #23 Analytical SOP References Table

Laboratory analytical SOP references for project-specific constituents of concern are listed in UFP QAPP Worksheet #30. Additionally, applicable Test America analytical SOPs have been included in Appendix 2 of this document.

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
DT-MET-016.0	*SW 6010A/B - Inductively Coupled Plasma- Atomic Emission Spectrometry, 9/14/07*	Definitive	Metals	ICP	Test America-Dayton	N
DT-MET-024.0	*SW 6020A - Inductively Coupled Plasma/Mass Spectrometry, 9/29/11*	Definitive	Metals	ICP/MS	Test America-Dayton	N
DT-MET-018.2	*Mercury*, 5/23/08	Definitive	Hg	Cold Vapor Atomic Absorption	Test America-Dayton	N
DT-WET-064.1	*Flash Point in Solids by Pensky - Martens Closed Cup Tester*, 7/30/2010	Definitive	Flashpoint	Pensky-Marten Closed Cup Tester	Test America-Dayton	N
DT-ORG-002.1	*Organo Chlorine Pesticides and PCBs by Gas Chromatography*, 4/30/10	Definitive	Pesticides	GC/ECD	Test America-Dayton	N
DT-WET-056.1	*Total Phosphorus and Orthophosphate*, 2/25/11	Definitive	Total Phosphorus	Spectrophotometer	Test America-Dayton	N
DT-WET-029.1	*Total Suspended Solids and Total Volatile*, 6/3/2011	Definitive	TSS	Drying Oven/ Analytical Balance	Test America-Dayton	N
DT-ORG-017.1	*Poly-Chlorinated Biphenyls*, 2/22/11	Definitive	PCB	GC/ECD	Test America-Dayton	N
DT-ORG-007.1	*Volatile Organic Compounds by GC/MS*, 3/31/11	Definitive	VOCs	GC/MS	Test America-Dayton	N
DT-ORG-008.1	*Base/ Neutral Acid Organics by GC/MS*, 7/21/11	Definitive	SVOC	GC/MS	Test America-Dayton	N
DT-ORG-015.1	*Pesticides*, 7/22/11	Definitive	Pesticides	GC/ECD	Test America-Dayton	N

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Worksheet #23 – continued

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
SOP Herbicides SAV	*Chlorinated Herbicides by GC/ECD*, 1/6/11	Definitive	Herbicides	GC/ECD	Test America-Savannah	N
DT-WET-019.1	*pH*, 3/29/10	Definitive	pH	pH meter	Test America-Dayton	N
DT-WET-020.1	*Paint Filter Liquids Test*, 12/15/09	Screening	Paint Filter	Paint Filter	Test America-Dayton	N
PE-IHD-002, Rev.1	*IH Air Method for Total And Respirable Dusts and Carbon Blank*, 8/27/10	Definitive	Total Particulates	Balance	Test America-Phoenix	N
PE-IHD-015, Rev1	*IH Air Monitoring Method for Polychlorobiphenyls*, 1/28/11	Definitive	PCB	GC/ECD	Test America-Phoenix	N
SA-GE-085, Rev. 7	*Sulfide: Titrimetric Preparation and Analysis*, 6/9/11	Definitive	Total Sulfide	N/A	Test America-Savannah	N
DT-WET-060.1	*Cyanide (Easy Chem)*, 6/30/10	Definitive	Total Cyanide	Systea Easy Chem Discrete Analyzer	Test America-Dayton	N

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QAPP Worksheet #24 Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
DataRam	Manufacturer				EQ Field Sampler	SP-Air-8
Turbidity Sensor	AutoCal	Daily prior to sample analysis	Turbidity		EQ Field Sampler	SP-Watr-1
ICP/MS	Initial Calibration (ICAL)	Daily prior to sample analysis	r ≥ 0.995	Repeat ICAL, if fail remake standards	Test America Analyst	DT-MET-024.0
	ICAL Verification (ICV)	After ICAL, prior to sample analysis	±10 Percent Difference (%D) RSD <5% for replicate injections	Repeat ICV, if fail repeat remake ICAL or ICV	Test America Analyst	
	Continuing Calibration Verification (CCV)	After every 10 samples and at end of run	±10 %D RSD <5% for replicate injections	Repeat CCV, if fail repeat ICAL	Test America Analyst	
ICP	Initial Calibration (ICAL)	Daily prior to sample analysis	r ≥ 0.995	Repeat ICAL, if fail remake standards	Test America Analyst	DT-MET-016.0
	ICAL Verification (ICV)	After ICAL, prior to sample analysis	±10 %D	Repeat ICV, if fail repeat remake ICAL or ICV	Test America Analyst	
	Continuing Calibration Verification (CCV)	After every 10 samples and end of run	±20 %D	Repeat CCV, if fail repeat ICAL	Test America Analyst	
AA	ICAL	Daily and with each batch	r ≥ 0.995	Repeat ICAL, if fail re-digest standards and samples	Test America Analyst	DT-MET-018.2
	ICV	After ICAL	±10 %D	Repeat ICV, if fail re-digest standards and samples	Test America Analyst	
	CCV	After each 10 samples and at end of run	±20 %D	Repeat CCV, if fail re-digest standards and samples	Test America Analyst	
GC/ECD PCBs	ICAL	Prior to first samples analyzed	RSD<20% or r ≥ 0.99	Repeat ICAL, if still fails re-pre standards	Test America Analyst	DT-ORG-017.1
	ICV	After ICAL, prior to sample analysis	±30 %D	Repeat ICV, if still fails re-prep standard or re-run ICAL	Test America Analyst	
	CCV	Prior to sample analysis and after each 24 hour shift	Aroclor 1242 (peak 1)–10%RSD Aroclor 1242 (peak 2)–15%RSD Aroclor 1242 (peak 3)–20%RSD Aroclor 1242 (peak 4)–12%RSD Aroclor 1242 (peak 5)–25%RSD Aroclor 1242 (Avg.)–16.4%RSD	Repeat CCV, re-prep standard, re-run ICAL if necessary	Test America Analyst	

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Worksheet #24 – continued

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
GC/ECD Pesticides/ PCBs	ICAL	Prior to first samples analyzed	RSD<10% or the r ≥ 0.99	Repeat ICAL, if still fails re-pre standards	Test America Analyst	DT-ORG-017.1
	ICV	After ICAL, prior to sample analysis	±30 %D	Repeat ICV, if still fails re-prep standard or re-run ICAL	Test America Analyst	
	CCV	Prior to sample analysis and after each 24 hour shift	±15 %D	Repeat CCV, re-prep standard, re-run ICAL if necessary	Test America Analyst	
GC/ECD Herbicides	ICAL	Prior to first samples analyzed	RSD<20% or the r ≥ 0.99	Repeat ICAL, if still fails re-pre standards	Test America Analyst	SOP Herbicides SAV
	ICV	After ICAL, prior to sample analysis	Avg. ±15 %D, no single analyte >45%	Repeat ICV, if still fails re-prep standard or re-run ICAL	Test America Analyst	
	CCV	Prior to sample analysis and after each 12 hour shift	Avg. ±15 %D, no single analyte >45%	Repeat CCV, re-prep standard, re-run ICAL if necessary	Test America Analyst	
GC/MS	ICAL	Prior to first samples analyzed	Minimum average RRF for the SPCCs[1] %RSD for CCCs <30%[2]	Repeat ICAL, if still fails re-pre standards	Test America Analyst	DT-ORG-007.1, DT-ORG-008.1,
	ICV	After ICAL, prior to sample analysis	±20 %D	Repeat ICV, if still fails re-prep standard or re-run ICAL	Test America Analyst	
	Bromofluorobenzene (BFB) Tuning	Prior to sample analysis and after each 12 hour shift	Criteria specified below[3]	Repeat, is still fails re-prep standard or re-run ICAL	Test America Analyst	
	CCV	Prior to sample analysis and after each 12 hour shift	SPCCs must meet minimum RRF CCCs <25%D	Repeat CCV, re-prep standard, re-run ICAL if necessary	Test America Analyst	
Spectrophoto meter	ICAL	Prior to first samples analyzed and only when necessary	r ≥ 0.995	Repeat analysis, re-prep standards	Test America Analyst	DT-WET-056.1
	ICV	After ICAL	±10 %D	Repeat analysis, re-prep standards	Test America Analyst	
	CCV	After every 10 samples and at end of run	±10 %D	Repeat analysis, re-prep standards	Test America Analyst	
Pensky-Marten Closed Cup	ICAL	Prior to first samples analyzed and 1 per batch	27.2 ±2°C	Repeat analysis, re-prep standards	Test America Analyst	DT-WET-015.1

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Worksheet #24 – continued

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference
Systea Easy chem discrete Analyzer	ICAL	Prior to first samples analyzed and 1/6 months	r ≥ 0.995	Repeat analysis, re-prep standards	Test America Analyst	DT-WET-060.1
	ICV	After ICAL	±10 %D	Repeat analysis, re-prep standards	Test America Analyst	
	CCV	After every 10 samples and at end of run	±10 %D	Repeat analysis, re-prep standards	Test America Analyst	
pH Meter	ICAL	Prior to sample analysis			Test America Analyst	DT-WET-019.1
	CCV		±1 pH unit	Recalibrate meter, if fail calibrate with 3 standards	Test America Analyst	

[1] Minimum Relative Response Factors (RRFs)for System Performance Check Compounds (SPCCs):
Chloromethane and 1,1-Dichloroethane – 0.10
Chlorobenzene and 1,1,2,2-Tetrachloroethane – 0.30
Bromoform - >0.10

[2] Calibration Check Compounds (CCCs) requiring % Relative Standard Deviation (RSD) of < 30: 1,1-Dichloroethene; Chloroform; 1,2-Dichloropropane; Toluene; Ehtylbenzene; Vinyl chloride

[3] Reference letter or number is from the Analytical SOP References table (Worksheet #23).

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

Instrument Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Action	Responsible Person	SOP Reference
ICP/MS			Check: peristaltic pump tubing for signs of wear; pump oil for proper level and quality (cleanliness); sampler and skimmer cones for cleanliness and proper orifice size	daily					DT-MET-024.1
			Check vacuum reading	daily	Low pressure indicates orifices are clogged High pressure indicates orifices are worn.				
	Clean torch components to remove accumulated deposits. Replace any cracked or worn o-rings.								
	Check RF coil for deformations or carbon buildup.								
			Check: spray pattern of the nebulizer; spray chamber for leaks at the connections; cleanliness of the spray chamber and condition of o-rings.	periodically					
			Check condition of filters and replace as necessary.	Monthly					

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Worksheet #25 – continued

Instrument Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Action	Responsible Person	SOP Reference
ICP			Check: peristaltic pump tubing for wear; argon humidifier to verify water level is between fill lines.	Daily					DT-MET-016.0
	Remove outer & inner quart tubes, injector tube, & spray chamber and clean. Wipe down quartz tubes & injector tube with 5% nitric acid solution, rinse with DI Water. Dissolve a couple of NaOH pellets in the spray chamber & rinse well with DI water to clean.			Once a week					
			Check spray chamber and torch body o-rings for signs of wear.	Once per month					
			Check load coil for signs of oxidation deposits.	periodically					
	Lubricate autosampler rails.			Once per month					
AA	Pack and Change Drying Tube		Check peristaltic pump tubing for signs of wear	Drying tube – with each startup Pump tubing - daily					DT-MET-018.2

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Worksheet #25 – continued

Instrument Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Action	Responsible Person	SOP Reference
GC/MS GC/ECD	Change septum and injection port liner.			daily					DT-ORG-007.1, DT-ORG-008.1, DT-ORG-015.1, DT-ORG-017.1, SOP Herbicides SAV
	Replace split disk and clipping/replacement of the guard column.				Breakdown of indicator compounds (see Section 15.1.1)	Replace split disk and clipping/replacement of guard column.			
	Clean MS.			Once per 6 months.					
			Check molecular/turbo pump oil.	Annually	Oil should be clear and level at 9±1 mm	Replace or add oil as necessary			
	Replace rough pump oil.			Annually					
pH Meter		Between uses store electrode in pH 4 buffer.	Check that the electrode is filled with 4 molar potassium chloride solution.	Before each use.					DT-WET-019.1
Flashpoint	Clean and rinse test cup.			After each sample.					DT-WET-015.1

[1]Reference letter or number is from the Analytical SOP References table (Worksheet #23)

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QAPP Worksheet #26 Sample Handling System

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
• Sample Collection (Personnel/Organization): EQ ERRS
• Sample Packaging (Personnel/Organization): EQ ERRS
• Coordination of Shipment (Personnel/Organization): Laboratory Procurement Coordinator, EQ ERRS
• Type of Shipment/Carrier: Federal Express, delivery, or courier pick-up
SAMPLE RECEIPT AND ANALYSIS
• Sample Receipt (Personnel/Organization): Laboratories Sample Login Personnel
• Sample Custody and Storage (Personnel/Organization): Laboratories Sample Receipt Personnel
• Sample Preparation (Personnel/Organization):): Laboratories Personnel
• Sample Determinative Analysis (Personnel/Organization):): Laboratories Personnel
SAMPLE ARCHIVING
• Field Sample Storage (No. of days from sample collection): All samples will be sent to the laboratory. The laboratory shall retain the samples in accordance with their laboratory SOPs.
• Sample Extract/Digestate Storage (No. of days from extraction/digestion): Six months
• Biological Sample Storage (No. of days from sample collection): Not Applicable
SAMPLE DISPOSAL
• Personnel/Organization: Laboratories Personnel
• Number of Days from Analysis: In accordance with the laboratory SOPs.

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QAPP Worksheet #27 Sample Custody Requirements

Chain-of-custody Procedures:
A Chain-of-Custody (COC) record will be maintained from the time the sample is collected until its delivery to the laboratory. To maintain a record of sample collection, transfer between personnel, shipment, and receipt by the laboratory, a COC record will be filled out for each sample at each sampling location. Each individual in possession of the samples must sign and date the sample COC document. Each time the samples are transferred, the signatures of the persons relinquishing and receiving the samples, as well as the date and time, will be documented. A copy of the COC is retained by the site leader for the site file. When samples (or groups of samples) are not under direct control of the individual responsible for them, they must be stored in a locked container sealed with a custody seal. The COC record will be considered completed upon receipt at the laboratory. The COC record should include (at minimum) the following:

- Type (s) of analysis(es) to be performed
- Sample ID number
- Sample information
- Sample station location
- Sample date
- Name(s) and signature(s) of sampler(s)
- Signature(s) of any individual(s) with control over samples

A separate COC form must accompany each cooler in each shipment. Within the laboratory, the person responsible for sample receipt must sign and date the COC form; verify that custody seals are intact on shipping containers; compare samples received against those listed on the COC form; examine all samples for possible shipping damage, leakage, and improper sample preservation; note on the COC record or laboratory receiving documentation that specific samples were damaged; notify sampling personnel as soon as possible so that appropriate samples may be resampled; verify that sample holding times have not been exceeded; maintain laboratory COC documentation; and place the samples in appropriate laboratory storage. If requested, the laboratory may submit internal COC documentation with the data package. Final sample disposition is completed according to laboratory license requirements.

Sample Identification Procedures:
All samples for analysis, including direct measurement samples and quality control samples, will be given a unique sample identification number. The sample numbers will be recorded in the field logbook, electronic files for the turbidity measurements, applicable sampling logs, the COC paperwork, and the shipment documents.

EQ ERRS will assign each sample a project sample number. The project samples will be identified according to the information presented in Worksheet 18.

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QAPP Worksheet #28 QC Samples Table

Worksheet #28-1

Matrix	Surface Water/Wastewater
Analytical Group	TSS
Concentration Level	Low
Sampling SOP	Worksheet #17
Analytical Method/ SOP Reference	2540D/DT-WET-029.1
Sampler's Name	ERRS
Field Sampling Organization	EQ
Analytical Organization	Test America-Dayton
No. of Sample Locations	TBD

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	1 per batch	RPD ≤ 10%	Flag associated data as estimated	Chemist	Laboratory Precision	See SOP in Appendix B
Method Blank	1 per batch	No target analyte concentrations above reporting limit	Flag data at less than 10 times the blank concentration as not detected	Chemist	Laboratory Contamination	See SOP in Appendix B

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Worksheet #28 – continued

Worksheet #28-2

Matrix	Surface Water/Wastewater
Analytical Group	PCBs
Concentration Level	Low
Sampling SOP	Worksheet #17
Analytical Method/ SOP Reference	608/DT-ORG-002.1
Sampler's Name	ERRS
Field Sampling Organization	EQ
Analytical Organization	Test America-Dayton
No. of Sample Locations	TBD

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	1 per batch	RPD ≤ 25%	Flag associated data as estimated	Chemist	Laboratory Precision	See SOP in Appendix B
Method Blank	1 per batch	No target analyte concentrations above reporting limit	Flag data at less than 10 times the blank concentration as not detected	Chemist	Laboratory Contamination	See SOP in Appendix B
LCS-Aroclor 1016	1 per batch	50-114 % R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
LCS-Aroclor 1260	1 per batch	8-127 % R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
Surrogates	2 per sample	DCB – 16-150% R TCMX – 22-145% R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
MS/MSD-Aroclor 1016	1 per batch	50-114 % R	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B
MS/MSD -Aroclor 1260	1 per batch	8-127 % R	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B

Worksheet #28-3

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Worksheet #28 – continued

Matrix	Surface Water/Wastewater
Analytical Group	Phosphorus
Concentration Level	Low
Sampling SOP	Worksheet #17
Analytical Method/ SOP Reference	4500P/DT-WET-056.1
Sampler's Name	ERRS
Field Sampling Organization	EQ
Analytical Organization	Test America-Dayton
No. of Sample Locations	TBD

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	1 per batch	RPD ≤ 20%	Flag associated data as estimated	Chemist	Laboratory Precision	See SOP in Appendix B
Method Blank	1 per batch	No target analyte concentrations above reporting limit	Flag data at less than 10 times the blank concentration as not detected	Chemist	Laboratory Contamination	See SOP in Appendix B
LCS	1 per batch	90 to 120 % R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
MS/MSD	1 per batch	86 to 115 % R	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B

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Worksheet #28 – continued

QAPP Worksheet #28-4

Matrix	Soil/Sediment
Analytical Group	PCBs
Concentration Level	Medium/Low
Sampling SOP	Worksheet #17
Analytical Method/ SOP Reference	SW846 8082/DT-ORG-017.1
Sampler's Name	ERRS
Field Sampling Organization	EQ
Analytical Organization	Test America-Dayton
No. of Sample Locations	233

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	1 per batch	RPD ≤ 25%	Flag associated data as estimated	Chemist	Laboratory Precision	See SOP in Appendix B
Method Blank	1 per batch	No target analyte concentrations above reporting limit	Flag data at less than 10 times the blank concentration as not detected	Chemist	Laboratory Contamination	See SOP in Appendix B
LCS-Aroclor 1016	1 per batch	20 to 150 % R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
LCS-Aroclor 1260	1 per batch	10 to 150 % R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
Surrogates	2 per sample	DCB – 15 to 150 %R TCMX – 10 to 150 %R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
LCS-Aroclor 1016	1 per batch	15 to 150 % R	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B
LCS-Aroclor 1260	1 per batch	10 to 150 % R	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B

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Worksheet #28 – continued

QAPP Worksheet #28-5

Matrix	Soil/Sediment
Analytical Group	Waste Characterization
Concentration Level	High/Medium/Low
Sampling SOP	Worksheet #17
Analytical Method/ SOP Reference	See Table 28-5a
Sampler's Name	ERRS
Field Sampling Organization	EQ
Analytical Organization	Test America-Savannah for Herbicides and Sulfide; Dayton for all others
No. of Sample Locations	TBD

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	1 per batch	See Table 28-5a	Flag associated data as estimated	Chemist	Laboratory Precision	See SOP in Appendix B
Method Blank	1 per batch	No target analyte concentrations above reporting limit	Flag data at less than 10 times the blank concentration as not detected	Chemist	Laboratory Contamination	See SOP in Appendix B
LCS	1 per batch	See Table 28-5a	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
Surrogates	See Table 28-5a	See Table 28-5a	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
MS/MSD	1 per batch	See Table 28-5a	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B

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Worksheet #28 – continued

Table 28-5a
Waste Characterization QC Acceptance Limits

Method	Analyte	Surr.	DUP	Matrix Spike		Blank Spike	
		%R	RPD	%R	RPD	%R	RPD
TCLP Metals by 1311/6000/7000 DT-ORG-003.2/DT-MET-016.0/DT-MET-018.2							
SW 6010B	Arsenic	-	-	75-125	20	80-120	15
SW 6010B	Barium	-	-	75-125	20	80-120	15
SW 6010B	Cadmium	-	-	75-125	20	80-120	15
SW 6010B	Chromium	-	-	75-125	20	80-120	15
SW 6010B	Lead	-	-	75-125	20	80-120	15
SW 6010B	Selenium	-	-	75-125	20	80-120	15
SW 6010B	Silver	-	-	75-125	20	80-120	15
SW 7470A	Mercury	-	10	75-125	20	80-120	-
TCLP Pesticides by EPA Method 1311/8081A DT-ORG-003.2/DT-ORG-015.1							
SW 8081	Methoxychlor	-	-	45-150	25	45-150	-
SW 8081	gamma-BHC (Lindane)	-	-	30-150	25	30-150	-
SW 8081	Chlordane	-	-	-	-	-	-
SW 8081	Endrin	-	-	30-150	25	30-150	-
SW 8081	Heptachlor	-	-	35-150	25	35-150	-
SW 8081	Heptachlor epoxide	-	-	42-150	25	42-150	-
SW 8081	Toxaphene	-	-	-	-	-	-
SW 8081	Tetrachloro-meta-xylene	14-150	-	-	-	-	-
SW 8081	Decachlorobiphenyl	12-150	-	-	-	-	-
TCLP Volatile Organic Compounds by EPA Method 1311/8260B DT-ORG-003.2/DT-ORG-007.1							
SW 8260B	Benzene	-	-	73-120	30	73-120	-
SW 8260B	2-Butanone (MEK)	-	-	72-120	30	72-120	-
SW 8260B	Carbon tetrachloride	-	-	64-122	30	64-122	-
SW 8260B	Chlorobenzene	-	-	67-121	30	67-121	-
SW 8260B	Chloroform	-	-	68-122	30	68-122	-
SW 8260B	1,2-Dichloroethane	-	-	70-120	30	70-120	-
SW 8260B	1,1-Dichloroethene	-	-	57-130	30	57-130	-
SW 8260B	Tetrachloroethene	-	-	58-133	30	58-133	-
SW 8260B	Trichloroethene	-	-	71-120	30	71-120	-
SW 8260B	Vinyl chloride	-	-	40-140	30	40-140	-
SW 8260B	1,2-Dichloroethane-d4	80-120	-	-	-	-	-

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Worksheet #28 – continued

Table 28-5a Waste Characterization QC Acceptance Limits – continued

Method	Analyte	Surr.	DUP	Matrix Spike		Blank Spike	
		%R	RPD	%R	RPD	%R	RPD
SW 8260B	Dibromofluoromethane	80-120	-	-	-	-	-
SW 8260B	Toluene-d8	80-120	-	-	-	-	-
SW 8260B	4-Bromofluorobenzene	80-120	-	-	-	-	-
TCLP Semivolatile Compounds by EPA Method 1311/8270C DT-ORG-003.2/DT-ORG-008.1							
SW 8270C	1,4-Dichlorobenzene	-	-	25-145	50	25-145	-
SW 8270C	2,4-Dinitrotoluene	-	-	35-150	50	35-150	-
SW 8270C	Hexachlorobenzene	-	-	30-150	50	30-150	-
SW 8270C	Hexachlorobutadiene	-	-	50-120	25	50-120	-
SW 8270C	Hexachloroethane	-	-	15-150	50	15-150	-
SW 8270C	2-Methylphenol (o-Cresol)	-	-	20-150	50	20-150	-
SW 8270C	3&4-Methylphenol (m&p Cresol)	-	-	25-150	50	25-150	-
SW 8270C	Nitrobenzene	-	-	25-150	50	25-150	-
SW 8270C	Pentachlorophenol	-	-	15-145	50	15-145	-
SW 8270C	Pyridine	-	-	31-120	25	31-120	-
SW 8270C	2,4,5-Trichlorophenol	-	-	25-150	50	25-150	-
SW 8270C	2,4,6-Trichlorophenol	-	-	25-150	50	25-150	-
SW 8270C	2-Fluorophenol	20-135	-	-	-	-	-
SW 8270C	Phenol-d6	20-150	-	-	-	-	-
SW 8270C	Nitrobenzene-d5	30-135	-	-	-	-	-
SW 8270C	2-Fluorobiphenyl	40-135	-	-	-	-	-
SW 8270C	2,4,6-Tribromophenol	25-145	-	-	-	-	-
SW 8270C	Terphenyl-d14	40-150	-	-	-	-	-
General Chemistry Parameters							
SW 1010(Mod)/ DT-WET-015.1	Ignitability by Flashpoint	-	-	-	-	-	-
SW 9012/ DT-WET-060.1	Cyanide, Total	-	-	75-123	25	75-123	-
SW 9034/ SOP Sulfide Soil SAV	Sulfide, Total	-	-				-
SW 9045D/ DT-WET-019.1	pH	-	-	-	-	98.6-101.4	-
SW 9095B/ DT-WET-020.1	Paint Filter Liquids	-	-	-	-	-	-

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Worksheet #28 – continued

QAPP Worksheet #28-6

Matrix	Soil – Staging Area
Analytical Group	VOCs, SVOCs. Pesticides, Herbicides, Metals, PCBs
Concentration Level	Low
Sampling SOP	Worksheet #17
Analytical Method/ SOP Reference	See Table 28-6a
Sampler's Name	ERRS
Field Sampling Organization	EQ
Analytical Organization	Test America-Dayton
No. of Sample Locations	TBD

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	1 per batch	See Table 28-6a	Flag associated data as estimated	Chemist	Laboratory Precision	See SOP in Appendix B
Method Blank	1 per batch	No target analyte concentrations above reporting limit	Flag data at less than 10 times the blank concentration as not detected	Chemist	Laboratory Contamination	See SOP in Appendix B
LCS	1 per batch	See Table 28-6a	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
Surrogates	See Table 28-6a	See Table 28-6a	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B
MS/MSD	1 per batch	See Table 28-6a	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B

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Worksheet #28 – continued

Table 28-6a
Support Areas QC Acceptance Limits

Method	Analyte	Surr.	DUP	Matrix Spike		Blank Spike	
		%R	RPD	%R	RPD	%R	RPD
Total Metals DT-MET-016.0/DT-MET-024.0/DT-MET-018.2							
SW 6010B	Aluminum	-	-	75-125	20	80-120	15
SW 6010B	Arsenic	-	-	75-125	20	80-120	15
SW 6010B	Barium	-	-	75-125	20	80-120	15
SW 6010B	Beryllium	-	-	75-125	20	80-120	15
SW 6010B	Cadmium	-	-	75-125	20	80-120	15
SW 6010B	Calcium	-	-	75-125	20	80-120	15
SW 6010B	Chromium	-	-	75-125	20	80-120	15
SW 6010B	Cobalt	-	-	75-125	20	80-120	15
SW 6010B	Iron	-	-	75-125	20	80-120	15
SW 6010B	Lead	-	-	75-125	20	80-120	15
SW 6010B	Magnesium	-	-	75-125	20	80-120	15
SW 6010B	Nickel	-	-	75-125	20	80-120	15
SW 6010B	Potassium	-	-	75-125	20	80-120	15
SW 6010B	Selenium	-	-	75-125	20	80-120	15
SW 6010B	Silver	-	-	75-125	20	80-120	15
SW 6010B	Sodium	-	-	75-125	20	80-120	15
SW 6010B	Vanadium	-	-	75-125	20	80-120	15
SW 6010B	Zinc	-	-	75-125	20	80-120	15
SW 6020A	Antimony	-	10	75-125	20	80-120	15
SW 6020A	Arsenic	-	10	75-125	20	80-120	15
SW 6020A	Copper	-	10	75-125	20	80-120	15
SW 6020A	Manganese	-	10	75-125	20	80-120	15
SW 6020A	Silver	-	10	75-125	20	80-120	15
SW 6020A	Thallium	-	10	75-125	20	80-120	15
SW 7471A	Mercury	-	10	75-125	20	80-120	15
Organochlorine Pesticides DT-ORG-015.1							
SW 8081	Aldrin	-	-	40-150	25	40-150	-
SW 8081	alpha-BHC	-	-	30-150	25	30-150	-
SW 8081	beta-BHC	-	-	10-150	25	10-150	-
SW 8081	gamma-BHC (Lindane)	-	-	30-150	25	30-150	-
SW 8081	delta-BHC	-	-	30-150	25	30-150	-
SW 8081	Chlordane	-	-	-	-	-	-
SW 8081	alpha-Chlordane	-	-	25-150	25	25-150	-

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Worksheet #28 – continued

Table 28-6a Support Areas QC Acceptance Limits – continued

Method	Analyte	Surr. %R	DUP RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike %R	Blank Spike RPD
SW 8081	gamma-Chlordane	-	-	30-150	25	30-150	-
SW 8081	Endrin ketone	-	-	15-150	-	15-150	-
SW 8081	Dieldrin	-	-	35-150	25	35-150	-
SW 8081	4,4'-DDD	-	-	35-150	25	35-150	-
SW 8081	4,4'-DDE	-	-	40-150	25	40-150	-
SW 8081	4,4'-DDT	-	-	15-150	25	15-150	-
SW 8081	Endosulfan I	-	-	35-150	25	35-150	-
SW 8081	Endosulfan II	-	-	10-150	25	10-150	-
SW 8081	Endosulfan sulfate	-	-	10-150	25	10-150	-
SW 8081	Endrin	-	-	15-150	25	15-150	-
SW 8081	Endrin aldehyde	-	-	15-150	25	15-150	-
SW 8081	Heptachlor	-	-	25-150	25	25-150	-
SW 8081	Heptachlor epoxide	-	-	35-150	25	35-150	-
SW 8081	Methoxychlor	-	-	10-150	25	10-150	-
SW 8081	Toxaphene	-	-	-	-	-	-
SW 8081	Tetrachloro-meta-xylene	15-150	-	-	-	-	-
SW 8081	Decachlorobiphenyl	10-150	-	-	-	-	-
PCBs DT-ORG-017.1							
SW 8082	PCB-1016	-	-	20-150	25	20-150	-
SW 8082	PCB-1221	-	-	-	-	-	-
SW 8082	PCB-1232	-	-	-	-	-	-
SW 8082	PCB-1242	-	-	-	-	-	-
SW 8082	PCB-1248	-	-	-	-	-	-
SW 8082	PCB-1254	-	-	-	-	-	-
SW 8082	PCB-1260	-	-	10-150	25	10-150	-
SW 8082	Tetrachloro-meta-xylene	15-150	-	-	-	-	-
SW 8082	Decachlorobiphenyl	10-150	-	-	-	-	-
Herbicides by EPA Method 8151A SOP Herbicide SAV							
SW8151A	2,4,5-T		50	32-130	50	32-130	50
SW8151A	2,4-D		50	47-130	50	47-130	50
SW8151A	2,4-DB						
SW8151A	Dalapon						
SW8151A	Dicamba						
SW8151A	Dichlorprop						
SW8151A	Dinoseb		50	10-130	50	10-130	50

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Worksheet #28 – continued

Table 28-6a Support Areas QC Acceptance Limits – continued

Method	Analyte	Surr. %R	DUP RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike %R	Blank Spike RPD
SW8151A	MCPA						
SW8151A	Mecoprop						
SW8151A	Pentachlorophenol		50	50-130	50	50-130	50
SW8151A	Silvex (2,4,5-TP)		50	24-130	50	24-130	50
SW8151A	DCAA	35-137					
Volatile Organic Compounds by GC/MS DT-ORG-007.1							
SW 8260A	Acetone	-	-	40-142	25	40-142	-
SW 8260A	Acrolein	-	-	46-135	30	46-135	-
SW 8260A	Acrylonitrile	-	-	57-125	30	57-125	-
SW 8260A	Allyl chloride	-	-	52-120	30	52-120	-
SW 8260A	Benzene	-	-	73-120	30	73-120	-
SW 8260A	Bromobenzene	-	-	70-120	30	70-120	-
SW 8260A	Bromochloromethane	-	-	69-125	30	69-125	-
SW 8260A	Bromodichloromethane (Dichlorobromomethane)	-	-	72-120	30	72-120	-
SW 8260A	Bromoform	-	-	61-120	30	61-120	-
SW 8260A	Bromomethane (Methyl bromide)	-	-	52-123	30	52-123	-
SW 8260A	2-Butanone (MEK)	-	-	72-120	30	72-120	-
SW 8260A	tert-Butylbenzene	-	-	72-120	30	72-120	-
SW 8260A	sec-Butylbenzene	-	-	72-120	30	72-120	-
SW 8260A	n-Butylbenzene	-	-	73-120	30	73-120	-
SW 8260A	Carbon disulfide	-	-	59-134	30	59-134	-
SW 8260A	Carbon tetrachloride	-	-	64-122	30	64-122	-
SW 8260A	Chlorobenzene	-	-	67-121	30	67-121	-
SW 8260A	Chloroethane	-	-	53-129	30	53-129	-
SW 8260A	2-Chloroethylvinyl ether	-	-	26-142	30	26-142	-
SW 8260A	Chloroform	-	-	68-122	30	68-122	-
SW 8260A	Chloromethane (Methyl chloride)	-	-	40-139	30	40-139	-
SW 8260A	Chloroprene	-	-	55-120	30	55-120	-
SW 8260A	4-Chlorotoluene	-	-	73-120	30	73-120	-
SW 8260A	2-Chlorotoluene	-	-	70-120	30	70-120	-
SW 8260A	Cyclohexane	-	-	-	-	-	-
SW 8260A	Dibromochloromethane (Chlorodibromomethane)	-	-	63-124	30	63-124	-
SW 8260A	1,2-Dibromo-3-chloropropane	-	-	74-120	30	74-120	-
SW 8260A	1,2-Dibromoethane (EDB)	-	-	69-120	30	69-120	-

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Worksheet #28 – continued

Table 28-6a Support Areas QC Acceptance Limits – continued

Method	Analyte	Surr. %R	DUP RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike %R	Blank Spike RPD
SW 8260A	Dibromomethane	-	-	76-120	30	76-120	-
SW 8260A	trans-1,4-Dichloro-2-butene	-	-	41-123	30	41-123	-
SW 8260A	1,2-Dichlorobenzene	-	-	74-120	30	74-120	-
SW 8260A	1,4-Dichlorobenzene	-	-	71-120	30	71-120	-
SW 8260A	1,3-Dichlorobenzene	-	-	72-120	30	72-120	-
SW 8260A	Dichlorodifluoromethane	-	-	10-274	30	10-274	-
SW 8260A	1,1-Dichloroethane	-	-	63-125	30	63-125	-
SW 8260A	1,2-Dichloroethane	-	-	70-120	30	70-120	-
SW 8260A	cis-1,2-Dichloroethene	-	-	73-120	30	73-120	-
SW 8260A	trans-1,2-Dichloroethene	-	-	70-120	30	70-120	-
SW 8260A	1,2-Dichloroethene (total)	-	-	-	-	-	-
SW 8260A	1,1-Dichloroethene	-	-	57-130	30	57-130	-
SW 8260A	1,3-Dichloropropane	-	-	72-120	30	72-120	-
SW 8260A	2,2-Dichloropropane	-	-	67-126	30	67-126	-
SW 8260A	1,2-Dichloropropane	-	-	68-120	30	68-120	-
SW 8260A	1,1-Dichloropropene	-	-	73-123	30	73-123	-
SW 8260A	cis-1,3-Dichloropropene	-	-	70-121	30	70-121	-
SW 8260A	1,3-Dichloropropene (total)	-	-	-	-	-	-
SW 8260A	trans-1,3-Dichloropropene	-	-	64-120	30	64-120	-
SW 8260A	Diethyl ether	-	-	60-121	30	60-121	-
SW 8260A	Ethyl acetate	-	-	10-148	30	10-148	-
SW 8260A	Ethylbenzene	-	-	69-123	30	69-123	-
SW 8260A	Ethyl methacrylate	-	-	62-120	30	62-120	-
SW 8260A	Hexachlorobutadiene	-	-	72-127	30	72-127	-
SW 8260A	n-Hexane	-	-	73-149	30	73-149	-
SW 8260A	2-Hexanone	-	-	60-120	30	60-120	-
SW 8260A	Iodomethane	-	-	36-127	30	36-127	-
SW 8260A	Isopropylbenzene (Cumene)	-	-	76-120	30	76-120	-
SW 8260A	p-Isopropyltoluene	-	-	71-121	30	71-121	-
SW 8260A	Methacrylonitrile	-	-	63-123	30	63-123	-
SW 8260A	Methyl tert-butyl ether	-	-	68-122	30	68-122	-
SW 8260A	Methylene chloride	-	-	46-124	30	46-124	-
SW 8260A	Methyl methacrylate	-	-	55-135	30	55-135	-
SW 8260A	2-Methylnaphthalene	-	-	-	-	-	-
SW 8260A	4-Methyl-2-pentanone (MIBK)	-	-	52-133	30	52-133	-
SW 8260A	Naphthalene	-	-	73-131	30	73-131	-

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Worksheet #28 – continued

Table 28-6a Support Areas QC Acceptance Limits – continued

Method	Analyte	Surr. %R	DUP RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike %R	Blank Spike RPD
SW 8260A	2-Nitropropane	-	-	54-126	30	54-126	-
SW 8260A	Pentachloroethane	-	-	68-125	30	68-125	-
SW 8260A	Propionitrile	-	-	63-133	30	63-133	-
SW 8260A	n-Propylbenzene	-	-	73-120	30	73-120	-
SW 8260A	Styrene	-	-	65-120	30	65-120	-
SW 8260A	1,1,1,2-Tetrachloroethane	-	-	64-126	30	64-126	-
SW 8260A	1,1,2,2-Tetrachloroethane	-	-	69-120	30	69-120	-
SW 8260A	Tetrachloroethene	-	-	58-133	30	58-133	-
SW 8260A	Toluene	-	-	63-126	30	63-126	-
SW 8260A	1,2,3-Trichlorobenzene	-	-	77-128	30	77-128	-
SW 8260A	1,2,4-Trichlorobenzene	-	-	75-128	30	75-128	-
SW 8260A	1,1,1-Trichloroethane	-	-	63-125	30	63-125	-
SW 8260A	1,1,2-Trichloroethane	-	-	71-120	30	71-120	-
SW 8260A	Trichloroethene	-	-	71-120	30	71-120	-
SW 8260A	Trichlorofluoromethane	-	-	60-128	30	60-128	-
SW 8260A	1,2,3-Trichloropropane	-	-	74-120	30	74-120	-
SW 8260A	1,1,2-Trichlorotrifluoroethane	-	-	-	-	-	-
SW 8260A	1,2,4-Trimethylbenzene	-	-	73-120	30	73-120	-
SW 8260A	1,3,5-Trimethylbenzene	-	-	71-120	30	71-120	-
SW 8260A	Vinyl Acetate	-	-	65-120	30	65-120	-
SW 8260A	Vinyl chloride	-	-	40-140	30	40-140	-
SW 8260A	m,p-Xylene	-	-	68-126	30	68-126	-
SW 8260A	o-Xylene	-	-	70-123	30	70-123	-
SW 8260A	Xylenes, Total	-	-	-	-	-	-
SW 8260A	1,2-Dichloroethane-d4	80-120	-	-	-	-	-
SW 8260A	Dibromofluoromethane	80-120	-	-	-	-	-
SW 8260A	Toluene-d8	80-120	-	-	-	-	-
SW 8260A	4-Bromofluorobenzene	80-120	-	-	-	-	-
Semivolatile Organics by GC/MS DT-ORG-008.1							
SW 8270C	Acenaphthene	-	-	30-150	50	30-150	-
SW 8270C	Acenaphthylene	-	-	35-150	50	35-150	-
SW 8270C	Acetophenone	-	-	-	-	-	-
SW 8270C	2-Acetylaminofluorene	-	-	-	-	-	-
SW 8270C	4-Aminobiphenyl	-	-	-	-	-	-
SW 8270C	Aniline	-	-	-	-	-	-

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Worksheet #28 – continued

Table 28-6a Support Areas QC Acceptance Limits – continued

Method	Analyte	Surr. %R	DUP RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike %R	Blank Spike RPD
SW 8270C	Anthracene	-	-	40-150	50	40-150	-
SW 8270C	Benzo (a) anthracene	-	-	40-150	50	40-150	-
SW 8270C	Benzo (b) fluoranthene	-	-	30-150	50	30-150	-
SW 8270C	Benzo (g,h,i) perylene	-	-	25-150	50	25-150	-
SW 8270C	Benzo (k) fluoranthene	-	-	35-150	50	35-150	-
SW 8270C	Benzo (a) pyrene	-	-	35-150	50	35-150	-
SW 8270C	Benzidine	-	-	10-152	50	10-152	-
SW 8270C	Benzyl alcohol	-	-	20-150	50	20-150	-
SW 8270C	Bis(2-chloroethoxy)methane	-	-	30-150	50	30-150	-
SW 8270C	Bis(2-chloroethyl)ether	-	-	20-150	50	20-150	-
SW 8270C	Bis(2-chloroisopropyl) ether	-	-	15-150	50	15-150	-
SW 8270C	Bis(2-ethylhexyl)phthalate	-	-	25-150	50	25-150	-
SW 8270C	4-Bromophenyl phenyl ether	-	-	35-150	50	35-150	-
SW 8270C	Butyl benzyl phthalate	-	-	30-150	50	30-150	-
SW 8270C	Carbazole	-	-	55-120	50	55-120	-
SW 8270C	4-Chloroaniline	-	-	15-150	50	15-150	-
SW 8270C	Chlorobenzilate	-	-	-	-	-	-
SW 8270C	4-Chloro-3-methylphenol	-	-	30-150	50	30-150	-
SW 8270C	2-Chloronaphthalene	-	-	30-150	50	30-150	-
SW 8270C	2-Chlorophenol	-	-	20-150	50	20-150	-
SW 8270C	4-Chlorophenyl phenyl ether	-	-	59-120	50	59-120	-
SW 8270C	Chrysene	-	-	30-150	50	30-150	-
SW 8270C	Diallate (cis or trans)	-	-	-	-	-	-
SW 8270C	Dibenzofuran	-	-	35-150	50	35-150	-
SW 8270C	1,2-Dichlorobenzene	-	-	20-150	50	20-150	-
SW 8270C	Dibenz (a,h) anthracene	-	-	25-150	50	25-150	-
SW 8270C	1,3-Dichlorobenzene	-	-	20-145	50	20-145	-
SW 8270C	1,4-Dichlorobenzene	-	-	25-145	50	25-145	-
SW 8270C	Di-n-butyl phthalate	-	-	64-123	50	64-123	-
SW 8270C	1,2-Diphenylhydrazine	-	-	-	-	-	-
SW 8270C	3,3'-Dichlorobenzidine	-	-	40-147	50	40-147	-
SW 8270C	2,4-Dichlorophenol	-	-	30-150	50	30-150	-
SW 8270C	2,6-Dichlorophenol	-	-	-	-	-	-
SW 8270C	Diethyl phthalate	-	-	35-150	50	35-150	-
SW 8270C	7,12-Dimethylbenz (a) anthracene	-	-	-	-	-	-
SW 8270C	Dimethoate	-	-	-	-	-	-

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Worksheet #28 – continued

Table 28-6a Support Areas QC Acceptance Limits – continued

Method	Analyte	Surr.	DUP	Matrix Spike		Blank Spike	
		%R	RPD	%R	RPD	%R	RPD
SW 8270C	Dimethylaminoazobenzene	-	-	-	-	-	-
SW 8270C	3,3'-Dimethylbenzidine	-	-	-	-	-	-
SW 8270C	2,4-Dimethylphenol	-	-	25-145	50	25-145	-
SW 8270C	Dimethyl phthalate	-	-	40-150	50	40-150	-
SW 8270C	1,3-Dinitrobenzene	-	-	-	-	-	-
SW 8270C	4,6-Dinitro-2-methylphenol	-	-	10-150	50	10-150	-
SW 8270C	2,4-Dinitrophenol	-	-	10-120	50	10-120	-
SW 8270C	2,6-Dinitrotoluene	-	-	35-150	50	35-150	-
SW 8270C	Di-n-octyl phthalate	-	-	35-150	50	35-150	-
SW 8270C	Diphenylamine	-	-	60-120	50	60-120	-
SW 8270C	Disulfoton	-	-	-	-	-	-
SW 8270C	Ethyl methanesulfonate	-	-	-	-	-	-
SW 8270C	Famphur	-	-	-	-	-	-
SW 8270C	Fluoranthene	-	-	35-150	50	35-150	-
SW 8270C	Fluorene	-	-	35-150	50	35-150	-
SW 8270C	Fluorene	-	-	35-150	50	35-150	-
SW 8270C	Hexachlorobenzene	-	-	30-150	50	30-150	-
SW 8270C	Hexachlorobutadiene	-	-	54-120	50	54-120	-
SW 8270C	Hexachlorocyclopentadiene	-	-	20-130	50	20-130	-
SW 8270C	Hexachloroethane	-	-	15-150	50	15-150	-
SW 8270C	Hexachloropropene	-	-	-	-	-	-
SW 8270C	Indeno (1,2,3-cd) pyrene	-	-	25-150	50	25-150	-
SW 8270C	Isodrin	-	-	-	-	-	-
SW 8270C	Isophorone	-	-	25-150	50	25-150	-
SW 8270C	Isosafrole	-	-	-	-	-	-
SW 8270C	Kepone	-	-	-	-	-	-
SW 8270C	Methapyrilene	-	-	-	-	-	-
SW 8270C	3-Methylcholanthrene	-	-	-	-	-	-
SW 8270C	1-Methylnaphthalene	-	-	-	-	-	-
SW 8270C	Methyl methanesulfonate	-	-	-	-	-	-
SW 8270C	2-Methylnaphthalene	-	-	30-150	50	30-150	-
SW 8270C	2-Methylphenol (o-Cresol)	-	-	20-150	50	20-150	-
SW 8270C	3&4-Methylphenol (m&p Cresol)	-	-	25-150	50	25-150	-
SW 8270C	Naphthalene	-	-	30-150	50	30-150	-
SW 8270C	1,4-Naphthoquinone	-	-	-	-	-	-
SW 8270C	1-Naphthylamine	-	-	-	-	-	-

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Worksheet #28 – continued

Table 28-6a Support Areas QC Acceptance Limits – continued

Method	Analyte	Surr.	DUP	Matrix Spike		Blank Spike	
		%R	RPD	%R	RPD	%R	RPD
SW 8270C	2-Naphthylamine	-	-	-	-	-	-
SW 8270C	2-Nitroaniline	-	-	59-120	50	59-120	-
SW 8270C	3-Nitroaniline	-	-	48-127	50	48-127	-
SW 8270C	4-Nitroaniline	-	-	55-131	50	55-131	-
SW 8270C	Nitrobenzene	-	-	25-150	50	25-150	-
SW 8270C	2-Nitrophenol	-	-	25-150	50	25-150	-
SW 8270C	2-Nitrophenol	-	-	25-150	50	25-150	-
SW 8270C	4-Nitrophenol	-	-	50-127	50	50-127	-
SW 8270C	5-Nitro-o-toluidine	-	-	-	-	-	-
SW 8270C	N-Nitrosodi-n-butylamine	-	-	-	-	-	-
SW 8270C	N-Nitrosodiethylamine	-	-	-	-	-	-
SW 8270C	N-Nitrosodimethylamine	-	-	48-120	50	48-120	-
SW 8270C	N-Nitrosomethylethylamine	-	-	-	-	-	-
SW 8270C	N-Nitrosodiphenylamine	-	-	60-120	50	60-120	-
SW 8270C	N-Nitrosodi-n-propylamine	-	-	20-150	50	20-150	-
SW 8270C	N-Nitrosopiperidine	-	-	-	-	-	-
SW 8270C	N-Nitrosopyrrolidine	-	-	-	-	-	-
SW 8270C	Parathion-ethyl	-	-	-	-	-	-
SW 8270C	Parathion-methyl	-	-	-	-	-	-
SW 8270C	Parathion	-	-	-	-	-	-
SW 8270C	Pentachlorobenzene	-	-	-	-	-	-
SW 8270C	Pentachlorophenol	-	-	15-145	50	15-145	-
SW 8270C	Pentachloronitrobenzene	-	-	-	-	-	-
SW 8270C	Phenacetin	-	-	-	-	-	-
SW 8270C	Phenanthrene	-	-	40-150	50	40-150	-
SW 8270C	Phenol	-	-	20-150	50	20-150	-
SW 8270C	1,4-Phenylenediamine	-	-	-	-	-	-
SW 8270C	Phorate	-	-	-	-	-	-
SW 8270C	2-Picoline	-	-	-	-	-	-
SW 8270C	Pronamide	-	-	-	-	-	-
SW 8270C	Pyrene	-	-	35-150	50	35-150	-
SW 8270C	Pyridine	-	-	45-120	50	45-120	-
SW 8270C	Safrole	-	-	-	-	-	-
SW 8270C	Sulfotepp	-	-	-	-	-	-
SW 8270C	1,2,4,5-Tetrachlorobenzene	-	-	-	-	-	-
SW 8270C	2,3,4,6-Tetrachlorophenol	-	-	-	-	-	-

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Worksheet #28 – continued

Table 28-6a Support Areas QC Acceptance Limits – continued

		Surr.	DUP	Matrix Spike		Blank Spike	
Method	**Analyte**	**%R**	**RPD**	**%R**	**RPD**	**%R**	**RPD**
SW 8270C	Thionazin	-	-	-	-	-	-
SW 8270C	o-Toluidine	-	-	-	-	-	-
SW 8270C	1,2,4-Trichlorobenzene	-	-	30-150	50	30-150	-
SW 8270C	2,4,5-Trichlorophenol	-	-	25-150	50	25-150	-
SW 8270C	2,4,6-Trichlorophenol	-	-	25-150	50	25-150	-
SW 8270C	O,O,O-Triethyl phosphorothioate	-	-	-	-	-	-
SW 8270C	1,3,5-Trinitrobenzene	-	-	-	-	-	-
SW 8270C	2-Fluorophenol	20-135	-	-	-	-	-
SW 8270C	Phenol-d6	20-150	-	-	-	-	-
SW 8270C	Nitrobenzene-d5	30-135	-	-	-	-	-
SW 8270C	2-Fluorobiphenyl	40-135	-	-	-	-	-
SW 8270C	2,4,6-Tribromophenol	25-145	-	-	-	-	-
SW 8270C	Terphenyl-d14	40-150	-	-	-	-	-

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Worksheet #28 – continued

QAPP Worksheet #28-7

Matrix	Solids – Borrow Source
Analytical Group	VOCs, SVOCs. Pesticides, Herbicides, Metals, PCBs
Concentration Level	Low
Sampling SOP	Worksheet #17
Analytical Method/ SOP Reference	See Table 28-6a
Sampler's Name	ERRS
Field Sampling Organization	EQ
Analytical Organization	Test America-Dayton
No. of Sample Locations	TBD

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	1 per batch	See Table 28-6a	Flag associated data as estimated	Chemist	Laboratory Precision	See SOP in Appendix B
Method Blank	1 per batch	No target analyte concentrations above reporting limit	Flag data at less than 10 times the blank concentration as not detected	Chemist	Laboratory Contamination	See SOP in Appendix B
LCS	1 per batch	See Table 28-6a	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
Surrogates	See Table 28-6a	See Table 28-6a	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B
MS/MSD	1 per batch	See Table 28-6a	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B

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Worksheet #28 – continued

Table 28-7a
Borrow Source QC Acceptance Limits

Method	Analyte	Surr.	DUP	Matrix Spike		Blank Spike	
		%R	RPD	%R	RPD	%R	RPD
Total Metals DT-MET-016.0/DT-MET-024.0/DT-MET-018.2							
SW 6010B	Aluminum	-	-	75-125	20	80-120	15
SW 6010B	Arsenic	-	-	75-125	20	80-120	15
SW 6010B	Barium	-	-	75-125	20	80-120	15
SW 6010B	Beryllium	-	-	75-125	20	80-120	15
SW 6010B	Cadmium	-	-	75-125	20	80-120	15
SW 6010B	Calcium	-	-	75-125	20	80-120	15
SW 6010B	Chromium	-	-	75-125	20	80-120	15
SW 6010B	Cobalt	-	-	75-125	20	80-120	15
SW 6010B	Iron	-	-	75-125	20	80-120	15
SW 6010B	Lead	-	-	75-125	20	80-120	15
SW 6010B	Magnesium	-	-	75-125	20	80-120	15
SW 6010B	Nickel	-	-	75-125	20	80-120	15
SW 6010B	Potassium	-	-	75-125	20	80-120	15
SW 6010B	Selenium	-	-	75-125	20	80-120	15
SW 6010B	Silver	-	-	75-125	20	80-120	15
SW 6010B	Sodium	-	-	75-125	20	80-120	15
SW 6010B	Vanadium	-	-	75-125	20	80-120	15
SW 6010B	Zinc	-	-	75-125	20	80-120	15
SW 6020A	Antimony	-	10	75-125	20	80-120	15
SW 6020A	Arsenic	-	10	75-125	20	80-120	15
SW 6020A	Copper	-	10	75-125	20	80-120	15
SW 6020A	Manganese	-	10	75-125	20	80-120	15
SW 6020A	Silver	-	10	75-125	20	80-120	15
SW 6020A	Thallium	-	10	75-125	20	80-120	15
SW 7471A	Mercury	-	10	75-125	20	80-120	15
Organochlorine Pesticides DT-ORG-015.1							
SW 8081	Aldrin	-	-	40-150	25	40-150	-
SW 8081	alpha-BHC	-	-	30-150	25	30-150	-
SW 8081	beta-BHC	-	-	10-150	25	10-150	-
SW 8081	gamma-BHC (Lindane)	-	-	30-150	25	30-150	-
SW 8081	delta-BHC	-	-	30-150	25	30-150	-
SW 8081	Chlordane	-	-	-	-	-	-
SW 8081	alpha-Chlordane	-	-	25-150	25	25-150	-

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Worksheet #28 – continued

Table 28-7a Borrow Source QC Acceptance Limits – continued

Method	Analyte	Surr. %R	DUP RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike %R	Blank Spike RPD
SW 8081	gamma-Chlordane	-	-	30-150	25	30-150	-
SW 8081	Endrin ketone	-	-	15-150	-	15-150	-
SW 8081	Dieldrin	-	-	35-150	25	35-150	-
SW 8081	4,4'-DDD	-	-	35-150	25	35-150	-
SW 8081	4,4'-DDE	-	-	40-150	25	40-150	-
SW 8081	4,4'-DDT	-	-	15-150	25	15-150	-
SW 8081	Endosulfan I	-	-	35-150	25	35-150	-
SW 8081	Endosulfan II	-	-	10-150	25	10-150	-
SW 8081	Endosulfan sulfate	-	-	10-150	25	10-150	-
SW 8081	Endrin	-	-	15-150	25	15-150	-
SW 8081	Endrin aldehyde	-	-	15-150	25	15-150	-
SW 8081	Heptachlor	-	-	25-150	25	25-150	-
SW 8081	Heptachlor epoxide	-	-	35-150	25	35-150	-
SW 8081	Methoxychlor	-	-	10-150	25	10-150	-
SW 8081	Toxaphene	-	-	-	-	-	-
SW 8081	Tetrachloro-meta-xylene	15-150	-	-	-	-	-
SW 8081	Decachlorobiphenyl	10-150	-	-	-	-	-
PCBs DT-ORG-017.1							
SW 8082	PCB-1016	-	-	20-150	25	20-150	-
SW 8082	PCB-1221	-	-	-	-	-	-
SW 8082	PCB-1232	-	-	-	-	-	-
SW 8082	PCB-1242	-	-	-	-	-	-
SW 8082	PCB-1248	-	-	-	-	-	-
SW 8082	PCB-1254	-	-	-	-	-	-
SW 8082	PCB-1260	-	-	10-150	25	10-150	-
SW 8082	Tetrachloro-meta-xylene	15-150	-	-	-	-	-
SW 8082	Decachlorobiphenyl	10-150	-	-	-	-	-
Herbicides by EPA Method 8151A SOP Herbicide SAV							
SW8151A	2,4,5-T		50	32-130	50	32-130	50
SW8151A	2,4-D		50	47-130	50	47-130	50
SW8151A	2,4-DB						
SW8151A	Dalapon						
SW8151A	Dicamba						
SW8151A	Dichlorprop						
SW8151A	Dinoseb		50	10-130	50	10-130	50

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Worksheet #28 – continued

Table 28-7a Borrow Source QC Acceptance Limits – continued

Method	Analyte	Surr. %R	DUP RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike %R	Blank Spike RPD
SW8151A	MCPA						
SW8151A	Mecoprop						
SW8151A	Pentachlorophenol		50	50-130	50	50-130	50
SW8151A	Silvex (2,4,5-TP)		50	24-130	50	24-130	50
SW8151A	DCAA	35-137					
Volatile Organic Compounds by GC/MS DT-ORG-007.1							
SW 8260A	Acetone	-	-	40-142	25	40-142	-
SW 8260A	Acrolein	-	-	46-135	30	46-135	-
SW 8260A	Acrylonitrile	-	-	57-125	30	57-125	-
SW 8260A	Allyl chloride	-	-	52-120	30	52-120	-
SW 8260A	Benzene	-	-	73-120	30	73-120	-
SW 8260A	Bromobenzene	-	-	70-120	30	70-120	-
SW 8260A	Bromochloromethane	-	-	69-125	30	69-125	-
SW 8260A	Bromodichloromethane (Dichlorobromomethane)	-	-	72-120	30	72-120	-
SW 8260A	Bromoform	-	-	61-120	30	61-120	-
SW 8260A	Bromomethane (Methyl bromide)	-	-	52-123	30	52-123	-
SW 8260A	2-Butanone (MEK)	-	-	72-120	30	72-120	-
SW 8260A	tert-Butylbenzene	-	-	72-120	30	72-120	-
SW 8260A	sec-Butylbenzene	-	-	72-120	30	72-120	-
SW 8260A	n-Butylbenzene	-	-	73-120	30	73-120	-
SW 8260A	Carbon disulfide	-	-	59-134	30	59-134	-
SW 8260A	Carbon tetrachloride	-	-	64-122	30	64-122	-
SW 8260A	Chlorobenzene	-	-	67-121	30	67-121	-
SW 8260A	Chloroethane	-	-	53-129	30	53-129	-
SW 8260A	2-Chloroethylvinyl ether	-	-	26-142	30	26-142	-
SW 8260A	Chloroform	-	-	68-122	30	68-122	-
SW 8260A	Chloromethane (Methyl chloride)	-	-	40-139	30	40-139	-
SW 8260A	Chloroprene	-	-	55-120	30	55-120	-
SW 8260A	4-Chlorotoluene	-	-	73-120	30	73-120	-
SW 8260A	2-Chlorotoluene	-	-	70-120	30	70-120	-
SW 8260A	Cyclohexane	-	-	-	-	-	-
SW 8260A	Dibromochloromethane (Chlorodibromomethane)	-	-	63-124	30	63-124	-
SW 8260A	1,2-Dibromo-3-chloropropane	-	-	74-120	30	74-120	-
SW 8260A	1,2-Dibromoethane (EDB)	-	-	69-120	30	69-120	-

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Worksheet #28 – continued

Table 28-7a Borrow Source QC Acceptance Limits – continued

Method	Analyte	Surr. %R	DUP RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike %R	Blank Spike RPD
SW 8260A	Dibromomethane	-	-	76-120	30	76-120	-
SW 8260A	trans-1,4-Dichloro-2-butene	-	-	41-123	30	41-123	-
SW 8260A	1,2-Dichlorobenzene	-	-	74-120	30	74-120	-
SW 8260A	1,4-Dichlorobenzene	-	-	71-120	30	71-120	-
SW 8260A	1,3-Dichlorobenzene	-	-	72-120	30	72-120	-
SW 8260A	Dichlorodifluoromethane	-	-	10-274	30	10-274	-
SW 8260A	1,1-Dichloroethane	-	-	63-125	30	63-125	-
SW 8260A	1,2-Dichloroethane	-	-	70-120	30	70-120	-
SW 8260A	cis-1,2-Dichloroethene	-	-	73-120	30	73-120	-
SW 8260A	trans-1,2-Dichloroethene	-	-	70-120	30	70-120	-
SW 8260A	1,2-Dichloroethene (total)	-	-	-	-	-	-
SW 8260A	1,1-Dichloroethene	-	-	57-130	30	57-130	-
SW 8260A	1,3-Dichloropropane	-	-	72-120	30	72-120	-
SW 8260A	2,2-Dichloropropane	-	-	67-126	30	67-126	-
SW 8260A	1,2-Dichloropropane	-	-	68-120	30	68-120	-
SW 8260A	1,1-Dichloropropene	-	-	73-123	30	73-123	-
SW 8260A	cis-1,3-Dichloropropene	-	-	70-121	30	70-121	-
SW 8260A	1,3-Dichloropropene (total)	-	-	-	-	-	-
SW 8260A	trans-1,3-Dichloropropene	-	-	64-120	30	64-120	-
SW 8260A	Diethyl ether	-	-	60-121	30	60-121	-
SW 8260A	Ethyl acetate	-	-	10-148	30	10-148	-
SW 8260A	Ethylbenzene	-	-	69-123	30	69-123	-
SW 8260A	Ethyl methacrylate	-	-	62-120	30	62-120	-
SW 8260A	Hexachlorobutadiene	-	-	72-127	30	72-127	-
SW 8260A	n-Hexane	-	-	73-149	30	73-149	-
SW 8260A	2-Hexanone	-	-	60-120	30	60-120	-
SW 8260A	Iodomethane	-	-	36-127	30	36-127	-
SW 8260A	Isopropylbenzene (Cumene)	-	-	76-120	30	76-120	-
SW 8260A	p-Isopropyltoluene	-	-	71-121	30	71-121	-
SW 8260A	Methacrylonitrile	-	-	63-123	30	63-123	-
SW 8260A	Methyl tert-butyl ether	-	-	68-122	30	68-122	-
SW 8260A	Methylene chloride	-	-	46-124	30	46-124	-
SW 8260A	Methyl methacrylate	-	-	55-135	30	55-135	-
SW 8260A	2-Methylnaphthalene	-	-	-	-	-	-
SW 8260A	4-Methyl-2-pentanone (MIBK)	-	-	52-133	30	52-133	-
SW 8260A	Naphthalene	-	-	73-131	30	73-131	-

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Worksheet #28 – continued

Table 28-7a Borrow Source QC Acceptance Limits – continued

Method	Analyte	Surr. %R	DUP RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike %R	Blank Spike RPD
SW 8260A	2-Nitropropane	-	-	54-126	30	54-126	-
SW 8260A	Pentachloroethane	-	-	68-125	30	68-125	-
SW 8260A	Propionitrile	-	-	63-133	30	63-133	-
SW 8260A	n-Propylbenzene	-	-	73-120	30	73-120	-
SW 8260A	Styrene	-	-	65-120	30	65-120	-
SW 8260A	1,1,1,2-Tetrachloroethane	-	-	64-126	30	64-126	-
SW 8260A	1,1,2,2-Tetrachloroethane	-	-	69-120	30	69-120	-
SW 8260A	Tetrachloroethene	-	-	58-133	30	58-133	-
SW 8260A	Toluene	-	-	63-126	30	63-126	-
SW 8260A	1,2,3-Trichlorobenzene	-	-	77-128	30	77-128	-
SW 8260A	1,2,4-Trichlorobenzene	-	-	75-128	30	75-128	-
SW 8260A	1,1,1-Trichloroethane	-	-	63-125	30	63-125	-
SW 8260A	1,1,2-Trichloroethane	-	-	71-120	30	71-120	-
SW 8260A	Trichloroethene	-	-	71-120	30	71-120	-
SW 8260A	Trichlorofluoromethane	-	-	60-128	30	60-128	-
SW 8260A	1,2,3-Trichloropropane	-	-	74-120	30	74-120	-
SW 8260A	1,1,2-Trichlorotrifluoroethane	-	-	-	-	-	-
SW 8260A	1,2,4-Trimethylbenzene	-	-	73-120	30	73-120	-
SW 8260A	1,3,5-Trimethylbenzene	-	-	71-120	30	71-120	-
SW 8260A	Vinyl Acetate	-	-	65-120	30	65-120	-
SW 8260A	Vinyl chloride	-	-	40-140	30	40-140	-
SW 8260A	m,p-Xylene	-	-	68-126	30	68-126	-
SW 8260A	o-Xylene	-	-	70-123	30	70-123	-
SW 8260A	Xylenes, Total	-	-	-	-	-	-
SW 8260A	1,2-Dichloroethane-d4	80-120	-	-	-	-	-
SW 8260A	Dibromofluoromethane	80-120	-	-	-	-	-
SW 8260A	Toluene-d8	80-120	-	-	-	-	-
SW 8260A	4-Bromofluorobenzene	80-120	-	-	-	-	-
Semivolatile Organics by GC/MS DT-ORG-008.1							
SW 8270C	Acenaphthene	-	-	30-150	50	30-150	-
SW 8270C	Acenaphthylene	-	-	35-150	50	35-150	-
SW 8270C	Acetophenone	-	-	-	-	-	-
SW 8270C	2-Acetylaminofluorene	-	-	-	-	-	-
SW 8270C	4-Aminobiphenyl	-	-	-	-	-	-
SW 8270C	Aniline	-	-	-	-	-	-

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Worksheet #28 – continued

Table 28-7a Borrow Source QC Acceptance Limits – continued

Method	Analyte	Surr.	DUP	Matrix Spike		Blank Spike	
		%R	RPD	%R	RPD	%R	RPD
SW 8270C	Cresol(s)	-	-	-	-	-	-
SW 8270C	Anthracene	-	-	40-150	50	40-150	-
SW 8270C	Benzo (a) anthracene	-	-	40-150	50	40-150	-
SW 8270C	Benzo (b) fluoranthene	-	-	30-150	50	30-150	-
SW 8270C	Benzo (g,h,i) perylene	-	-	25-150	50	25-150	-
SW 8270C	Benzo (k) fluoranthene	-	-	35-150	50	35-150	-
SW 8270C	Benzo (a) pyrene	-	-	35-150	50	35-150	-
SW 8270C	Benzidine	-	-	10-152	50	10-152	-
SW 8270C	Benzyl alcohol	-	-	20-150	50	20-150	-
SW 8270C	Bis(2-chloroethoxy)methane	-	-	30-150	50	30-150	-
SW 8270C	Bis(2-chloroethyl)ether	-	-	20-150	50	20-150	-
SW 8270C	Bis(2-chloroisopropyl) ether	-	-	15-150	50	15-150	-
SW 8270C	Bis(2-ethylhexyl)phthalate	-	-	25-150	50	25-150	-
SW 8270C	4-Bromophenyl phenyl ether	-	-	35-150	50	35-150	-
SW 8270C	Butyl benzyl phthalate	-	-	30-150	50	30-150	-
SW 8270C	Carbazole	-	-	55-120	50	55-120	-
SW 8270C	4-Chloroaniline	-	-	15-150	50	15-150	-
SW 8270C	Chlorobenzilate	-	-	-	-	-	-
SW 8270C	4-Chloro-3-methylphenol	-	-	30-150	50	30-150	-
SW 8270C	2-Chloronaphthalene	-	-	30-150	50	30-150	-
SW 8270C	2-Chlorophenol	-	-	20-150	50	20-150	-
SW 8270C	4-Chlorophenyl phenyl ether	-	-	59-120	50	59-120	-
SW 8270C	Chrysene	-	-	30-150	50	30-150	-
SW 8270C	Diallate (cis or trans)	-	-	-	-	-	-
SW 8270C	Dibenzofuran	-	-	35-150	50	35-150	-
SW 8270C	1,2-Dichlorobenzene	-	-	20-150	50	20-150	-
SW 8270C	Dibenz (a,h) anthracene	-	-	25-150	50	25-150	-
SW 8270C	1,3-Dichlorobenzene	-	-	20-145	50	20-145	-
SW 8270C	1,4-Dichlorobenzene	-	-	25-145	50	25-145	-
SW 8270C	Di-n-butyl phthalate	-	-	64-123	50	64-123	-
SW 8270C	1,2-Diphenylhydrazine	-	-	-	-	-	-
SW 8270C	3,3'-Dichlorobenzidine	-	-	40-147	50	40-147	-
SW 8270C	2,4-Dichlorophenol	-	-	30-150	50	30-150	-
SW 8270C	2,6-Dichlorophenol	-	-	-	-	-	-
SW 8270C	Diethyl phthalate	-	-	35-150	50	35-150	-
SW 8270C	7,12-Dimethylbenz (a) anthracene	-	-	-	-	-	-

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Worksheet #28 – continued

Table 28-7a Borrow Source QC Acceptance Limits – continued

Method	Analyte	Surr.	DUP	Matrix Spike		Blank Spike	
		%R	RPD	%R	RPD	%R	RPD
SW 8270C	Dimethoate	-	-	-	-	-	-
SW 8270C	Dimethylaminoazobenzene	-	-	-	-	-	-
SW 8270C	3,3'-Dimethylbenzidine	-	-	-	-	-	-
SW 8270C	2,4-Dimethylphenol	-	-	25-145	50	25-145	-
SW 8270C	Dimethyl phthalate	-	-	40-150	50	40-150	-
SW 8270C	1,3-Dinitrobenzene	-	-	-	-	-	-
SW 8270C	4,6-Dinitro-2-methylphenol	-	-	10-150	50	10-150	-
SW 8270C	2,4-Dinitrophenol	-	-	10-120	50	10-120	-
SW 8270C	2,6-Dinitrotoluene	-	-	35-150	50	35-150	-
SW 8270C	Di-n-octyl phthalate	-	-	35-150	50	35-150	-
SW 8270C	Diphenylamine	-	-	60-120	50	60-120	-
SW 8270C	Disulfoton	-	-	-	-	-	-
SW 8270C	Ethyl methanesulfonate	-	-	-	-	-	-
SW 8270C	Famphur	-	-	-	-	-	-
SW 8270C	Fluoranthene	-	-	35-150	50	35-150	-
SW 8270C	Fluorene	-	-	35-150	50	35-150	-
SW 8270C	Fluorene	-	-	35-150	50	35-150	-
SW 8270C	Hexachlorobenzene	-	-	30-150	50	30-150	-
SW 8270C	Hexachlorobutadiene	-	-	54-120	50	54-120	-
SW 8270C	Hexachlorocyclopentadiene	-	-	20-130	50	20-130	-
SW 8270C	Hexachloroethane	-	-	15-150	50	15-150	-
SW 8270C	Hexachloropropene	-	-	-	-	-	-
SW 8270C	Indeno (1,2,3-cd) pyrene	-	-	25-150	50	25-150	-
SW 8270C	Isodrin	-	-	-	-	-	-
SW 8270C	Isophorone	-	-	25-150	50	25-150	-
SW 8270C	Isosafrole	-	-	-	-	-	-
SW 8270C	Kepone	-	-	-	-	-	-
SW 8270C	Methapyrilene	-	-	-	-	-	-
SW 8270C	3-Methylcholanthrene	-	-	-	-	-	-
SW 8270C	1-Methylnaphthalene	-	-	-	-	-	-
SW 8270C	Methyl methanesulfonate	-	-	-	-	-	-
SW 8270C	2-Methylnaphthalene	-	-	30-150	50	30-150	-
SW 8270C	2-Methylphenol (o-Cresol)	-	-	20-150	50	20-150	-
SW 8270C	3&4-Methylphenol (m&p Cresol)	-	-	25-150	50	25-150	-
SW 8270C	Naphthalene	-	-	30-150	50	30-150	-
SW 8270C	1,4-Naphthoquinone	-	-	-	-	-	-

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Worksheet #28 – continued

Table 28-7a Borrow Source QC Acceptance Limits – continued

Method	Analyte	Surr.	DUP	Matrix Spike		Blank Spike	
		%R	RPD	%R	RPD	%R	RPD
SW 8270C	1-Naphthylamine	-	-	-	-	-	-
SW 8270C	2-Naphthylamine	-	-	-	-	-	-
SW 8270C	2-Nitroaniline	-	-	59-120	50	59-120	-
SW 8270C	3-Nitroaniline	-	-	48-127	50	48-127	-
SW 8270C	4-Nitroaniline	-	-	55-131	50	55-131	-
SW 8270C	Nitrobenzene	-	-	25-150	50	25-150	-
SW 8270C	2-Nitrophenol	-	-	25-150	50	25-150	-
SW 8270C	2-Nitrophenol	-	-	25-150	50	25-150	-
SW 8270C	4-Nitrophenol	-	-	50-127	50	50-127	-
SW 8270C	5-Nitro-o-toluidine	-	-	-	-	-	-
SW 8270C	N-Nitrosodi-n-butylamine	-	-	-	-	-	-
SW 8270C	N-Nitrosodiethylamine	-	-	-	-	-	-
SW 8270C	N-Nitrosodimethylamine	-	-	48-120	50	48-120	-
SW 8270C	N-Nitrosomethylethylamine	-	-	-	-	-	-
SW 8270C	N-Nitrosodiphenylamine	-	-	60-120	50	60-120	-
SW 8270C	N-Nitrosodi-n-propylamine	-	-	20-150	50	20-150	-
SW 8270C	N-Nitrosopiperidine	-	-	-	-	-	-
SW 8270C	N-Nitrosopyrrolidine	-	-	-	-	-	-
SW 8270C	Parathion-ethyl	-	-	-	-	-	-
SW 8270C	Parathion-methyl	-	-	-	-	-	-
SW 8270C	Parathion	-	-	-	-	-	-
SW 8270C	Pentachlorobenzene	-	-	-	-	-	-
SW 8270C	Pentachlorophenol	-	-	15-145	50	15-145	-
SW 8270C	Pentachloronitrobenzene	-	-	-	-	-	-
SW 8270C	Phenacetin	-	-	-	-	-	-
SW 8270C	Phenanthrene	-	-	40-150	50	40-150	-
SW 8270C	Phenol	-	-	20-150	50	20-150	-
SW 8270C	1,4-Phenylenediamine	-	-	-	-	-	-
SW 8270C	Phorate	-	-	-	-	-	-
SW 8270C	2-Picoline	-	-	-	-	-	-
SW 8270C	Pronamide	-	-	-	-	-	-
SW 8270C	Pyrene	-	-	35-150	50	35-150	-
SW 8270C	Pyridine	-	-	45-120	50	45-120	-
SW 8270C	Safrole	-	-	-	-	-	-
SW 8270C	Sulfotepp	-	-	-	-	-	-
SW 8270C	1,2,4,5-Tetrachlorobenzene	-	-	-	-	-	-

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Worksheet #28 – continued

Table 28-7a Borrow Source QC Acceptance Limits – continued

Method	Analyte	Surr.	DUP	Matrix Spike		Blank Spike	
		%R	RPD	%R	RPD	%R	RPD
SW 8270C	2,3,4,6-Tetrachlorophenol	-	-	-	-	-	-
SW 8270C	Thionazin	-	-	-	-	-	-
SW 8270C	o-Toluidine	-	-	-	-	-	-
SW 8270C	1,2,4-Trichlorobenzene	-	-	30-150	50	30-150	-
SW 8270C	2,4,5-Trichlorophenol	-	-	25-150	50	25-150	-
SW 8270C	2,4,6-Trichlorophenol	-	-	25-150	50	25-150	-
SW 8270C	O,O,O-Triethyl phosphorothioate	-	-	-	-	-	-
SW 8270C	1,3,5-Trinitrobenzene	-	-	-	-	-	-
SW 8270C	2-Fluorophenol	20-135	-	-	-	-	-
SW 8270C	Phenol-d6	20-150	-	-	-	-	-
SW 8270C	Nitrobenzene-d5	30-135	-	-	-	-	-
SW 8270C	2-Fluorobiphenyl	40-135	-	-	-	-	-
SW 8270C	2,4,6-Tribromophenol	25-145	-	-	-	-	-
SW 8270C	Terphenyl-d14	40-150	-	-	-	-	-

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Worksheet #28 – continued

QAPP Worksheet #28-8

Matrix	Air
Analytical Group	PCBs & Particulates
Concentration Level	Low
Sampling SOP	Worksheet #17
Analytical Method/ SOP Reference	SOP
Sampler's Name	ERRS
Field Sampling Organization	EQ
Analytical Organization	Test America-Phoenix
No. of Sample Locations	TBD

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	1	RPD ≤ 20%	Flag associated data as estimated	Chemist	Laboratory Precision	See SOP in Appendix B
Method Blank	1	No target analyte concentrations above reporting limit	Flag data at <10 times blank concentration ND	Chemist	Laboratory Contamination	See SOP in Appendix B
LCS	1	85 to 115 % Recovery	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B

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QAPP Worksheet #29 Project Documents and Records Table

Sample Collection Documents and Records	On-site Analysis Documents and Records	Off-site Analysis Documents and Records	Data Assessment Documents and Records	Other
Logbook(s)	Logbook(s)	Sample Receipt, Custody, and Tracking Records	Data Validation Reports	OSC After-Action Report
Sampling Logs	Instrument printouts (raw data)	Preliminary analytical data reports	Corrective Action Reports	
Chain-of-Custody Forms	Final Analytical Data Summary Report	Final Analytical Data Summary Reports		
Photos	Equipment Calibration Logs	Laboratory Electronic Data Deliverables		
GPS Coordinates		Equipment Calibration Logs		
Airbills		Sample Preparation Logs		
Field Diagrams		Run Logs		
		Equipment Maintenance, Testing, and Inspection Logs		
		Instrument printouts (raw data)		
		Quality Control Sample Summary Forms		
		Sample Disposal Records		
		Corrective Action Reports		

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QAPP Worksheet #30 Analytical Services Table

Matrix	Analytical Group	Concentration Level	Sample Locations/ID Numbers[1]	Analytical SOP	Data Package Turnaround Time	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)[2]	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Surface Water/ Wastewater	TSS, PCB and Total Phosphorus	Low	See Worksheet #19	See Worksheet 12-1	5 Working Days	Test America 4738 Gateway Circle Dayton, OH 45440 Taryn M. Mancine (937) 294-6856	Test America 4101 Shuffel Street NW North Canton, OH 44720 330.497.9396 or 2417 Bond Street University Park, IL 60484 708.534.5200
Sediment	PCB	Low/Medium	See Worksheet #19	See Worksheet 12-2 & 12-3	5 Working Days		
Sediment/Soil	Waste Characterization	High	See Worksheet #19	See Worksheet 12-4	5 Working Days		
Soil (Staging/Support Areas Pre and Post Construction)	VOCs, SVOCs, Metals, Pesticides/PCB, Herbicides	Medium	See Worksheet #19	See Worksheet 12-5	5 Working Days		
Borrow Source - Backfill (Gravel, soil, and Sand)	VOCs, SVOCs, Metals, Pesticides/PCB, Herbicides	Low	See Worksheet #19	See Worksheet 12-6	5 Working Days		
Air	PCB and Particulates	Low	See Worksheet #19	See Worksheet 12-7	5 Working Days	4625 East Cotton Center Boulevard Suite 189 Phoenix, AZ 85040 602.437.3340	

Notes:
[1] See Worksheet #27 for a description of sample numbers to be used.
[2] Test America Savannah will be performing analysis for Sulfides and Herbicides.
Savannah Lab
5102 LaRoche Avenue
Savannah, GA 31404
912.354.7858

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QAPP Worksheet #31 Planned Project Assessments Table

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 Actions (CA) (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (Title and Organizational Affiliation)
Not Applicable – A field audit is not planned for this removal project.							

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QAPP Worksheet #32 Assessment Findings and Response Actions

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, Org.)	Timeframe for Response
Not Applicable – A field audit is not planned for this removal project.						

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QAPP Worksheet #33 QA Management Reports Table

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	To be prepared following receipt of an analytical data package	Three weeks following receipt of final data package from laboratory	EQ or START Chemist. WESTON will perform a compliance check of the data.	Sam Borries, USEPA OSC
Final Project Report	To be prepared following receipt of all analytical data validation reports	One month following receipt of all data validation reports	EQ Response Manager	Sam Borries, USEPA OSC
Monthly Report	Every month for the prior month activities, as needed	20th of month for the prior month activities	EQ Response Manager	Sam Borries, USEPA OSC

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QAPP Worksheet #34 Sampling and Analysis Verification (Step I) Process Table

Verification Input	Description	Internal/ External	Responsible for Verification (Name, Organization)
COC Forms	The Site Leader will submit COC forms to the project manager within 24 hours following all sample shipments to the laboratory. The Project Manager will review the COC forms for completeness to ensure that the proper analyses are being performed.	Internal	Jackie Doan, Sample Management Coordinator, EQM ERRS
Logbook	The Response Manager will review the logbook for accuracy and completeness following field sampling activities.	Internal	EQ Site Sample Coordinator, EQM ERRS
Laboratory Data	All laboratory data will be verified by the QA officer of the laboratory performing the sample analyses. The laboratory data will be validated in accordance with the procedures described in Worksheet #s 35 and 36. WESTON will perform a compliance check of all data reviewed by the ERRS or START Chemist.	Internal External	QA Officer, Laboratory ERRS or START Chemist

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QAPP Worksheet #35 Sampling and Analysis Validation (Steps IIa and IIb) Process Table

Stage/ % Validation	Validation Input	Description	Responsible for Validation
IIa / 100%	SOPs and logbook	The RM/Site Manager will ensure that all SOPs were followed in the field through daily conversations with the site leader and review of the site logbook.	Eric Bowman, Site Manager, EQM ERRS
Post-excavation Sampling – Portage Creek Removal Slope Areas			
IIa / 100%	Preliminary Data and Final Analytical Data Package	The Sample Management Coordinator will review the preliminary data and final analytical data package to ensure that all analyses requested were received and to ensure that required project quantitation limits were met. LDC's ADR tool will be utilized to perform this review.	Jackie Doan, EQM ERRS
IV / 10%	Final Analytical Data Package	The data validator will perform data validation of the final analytical data package to ensure that all QC requirements specified in the QAPP were met. WESTON will perform a compliance check of all validated data.	ERRS or START Chemist
Surface Soil Sampling – Upjohn Park			
IIa / 100%	Preliminary Data and Final Analytical Data Package	The Sample Management Coordinator will review the preliminary data and final analytical data package to ensure that all analyses requested were received and to ensure that required project quantitation limits were met. LDC's ADR tool will be utilized to perform this review.	Jackie Doan, EQM ERRS
IV / 10%	Final Analytical Data Package	The data validator will perform data validation of the final analytical data package to ensure that all QC requirements specified in the QAPP were met. WESTON will perform a compliance check of all validated data.	ERRS or START Chemist
Pre-Removal/Data PCB Gap Sediment Sampling – Portage Creek Select Grids in the Removal Slope Areas			
IIa / 100%	Preliminary Data and Final Analytical Data Package	The Sample Management Coordinator will review the preliminary data and final analytical data package to ensure that all analyses requested were received and to ensure that required project quantitation limits were met. LDC's ADR tool will be utilized to perform this review.	Jackie Doan, EQM ERRS
IIb / 10%	Final Analytical Data Package	The data validator will perform data validation of the final analytical data package to ensure that all QC requirements specified in the QAPP were met. WESTON will perform a compliance check of all validated data.	ERRS or START Chemist
Waste Characterization Sampling			
IIa / 100%	Preliminary Data and Final Analytical Data Package	The Sample Management Coordinator will review the preliminary data and final analytical data package to ensure that all analyses requested were received and to ensure that required project quantitation limits were met.	Jackie Doan, EQM ERRS
IIa / 100%	Final Analytical Data Package	The data validator will perform data validation of the final analytical data package to ensure that all QC requirements specified in the QAPP were met. WESTON will perform a compliance check of all validated data.	Jackie Doan, EQM ERRS

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Worksheet #35 – continued

Stage/ % Validation	Validation Input	Description	Responsible for Validation
Surface Water Sampling – Portage Creek / Wastewater Treatment Sampling			
IIa / 100%	Preliminary Data and Final Analytical Data Package	The Sample Management Coordinator will review the preliminary data and final analytical data package to ensure that all analyses requested were received and to ensure that required project quantitation limits were met. LDC's ADR tool will be utilized to perform this review.	Jackie Doan, EQM ERRS
IIb / 10%	Final Analytical Data Package	The data validator will perform data validation of the final analytical data package to ensure that all QC requirements specified in the QAPP were met. WESTON will perform a compliance check of all validated data.	ERRS or START Chemist
Personnel and Area Monitoring Sampling			
IIa / 100%	Preliminary Data and Final Analytical Data Package	The Sample Management Coordinator will review the preliminary data and final analytical data package to ensure that all analyses requested were received and to ensure that required project quantitation limits were met.	Jackie Doan, EQM ERRS
IIa / 100%	Final Analytical Data Package	The data validator will perform data validation of the final analytical data package to ensure that all QC requirements specified in the QAPP were met. WESTON will perform a compliance check of all validated data.	Jackie Doan, EQM ERRS
Pre- and Post-Construction Sampling – Support Areas			
IIa / 100%	Preliminary Data and Final Analytical Data Package	The Sample Management Coordinator will review the preliminary data and final analytical data package to ensure that all analyses requested were received and to ensure that required project quantitation limits were met. LDC's ADR tool will be utilized to perform this review.	Jackie Doan, EQM ERRS
IIb / 10%	Final Analytical Data Package	The data validator will perform data validation of the final analytical data package to ensure that all QC requirements specified in the QAPP were met. WESTON will perform a compliance check of all validated data.	ERRS or START Chemist
Borrow Source Sampling - Backfill			
IIa / 100%	Preliminary Data and Final Analytical Data Package	The Sample Management Coordinator will review the preliminary data and final analytical data package to ensure that all analyses requested were received and to ensure that required project quantitation limits were met. LDC's ADR tool will be utilized to perform this review.	Jackie Doan, EQM ERRS
IIb / 10%	Final Analytical Data Package	The data validator will perform data validation of the final analytical data package to ensure that all QC requirements specified in the QAPP were met. WESTON will perform a compliance check of all validated data.	ERRS or START Chemist

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QAPP Worksheet #36 Sampling and Analysis Validation (Steps IIa and IIb) Summary Table

Stage	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)
Pre-Removal/Data Gap PCB Sampling – `Portage Creek Select Grids in the Removal Slope Areas					
IIa / IIb	soil/sediment	PCBs	Medium	U.S. EPA CLP NFG for Inorganic Data	ERRS / START Chemist
Surface Soil Sampling – Upjohn Park					
IIa / IV	soil	PCBs	Low	U.S. EPA CLP NFG for Inorganic Data	ERRS / START Chemist
Pre- and Post-Construction Sampling – Support Areas					
IIa / IIb	soils	TCL VOCs, TCL SVOCs, TCL Pesticides, TCL Herbicides, PCBs, TAL metals	Medium	U.S. EPA CLP NFG for Inorganic Data	ERRS / START Chemist
Waste Characterization Sampling					
IIa	soils	Waste Characterization	High	U.S. EPA CLP NFG for Inorganic Data	ERRS Chemist
Borrow Source Sampling - Backfill					
IIa / IIb	solids	TCL VOCs, TCL SVOCs, TCL Pesticides, TCL Herbicides, PCBs, TAL metals	Low	U.S. EPA CLP NFG for Inorganic Data	ERRS / START Chemist
Personnel and Area Monitoring Sampling					
IIa	Air	PCBs, total particulates	Low	U.S. EPA CLP NFG for Inorganic Data	ERRS Chemist
Surface Water Sampling – Portage Creek / Wastewater Treatment Sampling					
IIa / IIb	surface water	PCBs, TSS, phosphorus	Medium	U.S. EPA CLP NFG for Inorganic Data	ERRS / START Chemist
Post-excavation Sampling – Portage Creek Removal Slope Areas					
IIa / IV	soil/sediment	PCBs	Low	U.S. EPA CLP NFG for Inorganic Data	ERRS / START Chemist

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QAPP Worksheet #37 Data Usability Assessment

Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used: Data, whether generated in the field or by the laboratory, are tabulated and reviewed for precision, accuracy, representativeness, and completeness by the site leader for field data or by the data validator for laboratory data from a fixed laboratory. The review of these data quality indicators (DQI) will compare the DQI with the data quality objects (DQO) detailed in the project-specific QAPP and in the analytical methods used.

Questions about data, as observed during the data review process, are resolved by contacting the respective site personnel and laboratories for resolution. All communications are documented including the resolution to the observed deficiencies. The original data and deliverables are kept in the Technical Direction Document (TDD) file.

When the data do not meet the project DQOs, WESTON START will investigate the root cause to the deficiency. Reasons may include laboratory operation, such as the laboratory's failure to adjust the extraction weight on high-moisture-content soil, failure of laboratory reporting limits to meet site Action Limits, or poor correlation between field screening and laboratory results. In these situations, WESTON START will discuss corrective actions with the OSC. These actions may include:

- Resampling for all or some of the parameters
- Preparing a technical memorandum to the site file, detailing limitations to the data
- Validating the data at a higher tier level to better qualify the results
- Preparing a technical memorandum determining the bias of field results

Describe the evaluative procedures used to assess overall measurement error associated with the project: The following specific items will be assessed in the manner described below:

Precision – Results of all laboratory duplicates and field duplicates will be presented in the laboratory data validation report. For each duplicate pair, the relative percent difference (RPD) will be calculated for each analyte with results greater than or equal to the quantitation limit. The RPDs will be checked against the measurement performance criteria presented on Worksheet #12A. The RPDs exceeding criteria will be identified on the tables in the final report with appropriate qualifiers. A discussion will follow summarizing the results of the laboratory precision. Any conclusions about the precision of the analyses will be drawn and any limitations on the use of the data will be described in the final report.

Accuracy/Bias Contamination – Results for all laboratory method blanks and instrument blanks will be presented in the laboratory data validation report. The results for each analyte will be checked against the measurement performance criteria presented on Worksheet #12A.

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Worksheet #37 – continued

Results for analytes that exceed criteria will be identified on the tables in the final report with appropriate qualifiers. A discussion will follow summarizing the results of the laboratory accuracy/bias. Any conclusions about the accuracy/bias of the analyses based on contamination will be drawn and any limitations on the use of the data will be described.

Overall Accuracy/Bias – The results for the continuing calibration standards will be presented in the laboratory case narrative. These results will be compared to the requirements listed on Worksheet #12A. A discussion will follow summarizing overall accuracy/bias. Any conclusions about the overall accuracy/bias of the analyses will be drawn and any limitations on the use of the data will be described.

Sensitivity – All sample results for monitoring well samples will be presented in tabular format. The sample results for each analyte will be checked against the method detection limits. Results for analytes that do not meet the contract required quantitation limits will be discussed. Any conclusions about the sensitivity of the analyses will be drawn and any limitations on the use of the data will be described.

Representativeness – Representativeness will be maintained by the site leader who will ensure that all sampling personnel are adhering to the sampling procedures dictated in the field sampling plan. In addition, the project manager will be in close contact with the field team leader to ensure that proper sampling techniques are being followed. Any conclusions about the representativeness of the sampling will be drawn and any limitations on the use of the data will be described.

Completeness – A completeness check will be done on all samples collected in the field and data generated by the laboratory. Completeness criteria are presented on Worksheet #12A. Completeness will be calculated as follows. For each sample collected, completeness will be calculated as the number of samples collected and number of analyses performed, divided by the total number of planned sample collection points and analyses. A discussion will follow summarizing the calculation of data completeness. Any conclusions about the completeness of the data for each analyte will be drawn and any limitations on the use of the data will be described.

Reconciliation – Each of the project quality objectives presented on Worksheet #12A will be examined to determine if the objective was met. Each analysis will first be evaluated in terms of the major impacts observed from the data validation, DQIs, and measurement performance criteria assessments. Based on the results of these assessments, the quality of the data will be determined. Based on the quality determined, the usability of the data for each analysis will be determined. Based on the usability of the data from all analyses for an objective, it will be determined if the project quality objective was met. The final report will include a summary of all the points that went into the reconciliation of each objective. As part of the reconciliation of each objective, conclusions will be drawn and any limitations on the usability of any of the data will be described.

Identify the personnel responsible for performing the usability assessment: The site leader will determine the usability of field data. The ERRS or START Chemist will validate the data and the ERRS or WESTON Sample Management Coordinator will do a compliance check of the

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Worksheet #37 – continued

data to determine the usability of analytical data. The Project Manager, Sarah Meyer, will be responsible for the overall usability to meet project objectives.

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: A data validation report will be prepared. Overall usability of data to meet project objectives will be described in the final report to be prepared by the Project Manager.

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References

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USEPA Field Environmental Decision Support. 2011b. *Portage Creek Core Displays of PCB Concentrations.* 14 April.

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APPENDIX A

FIGURES

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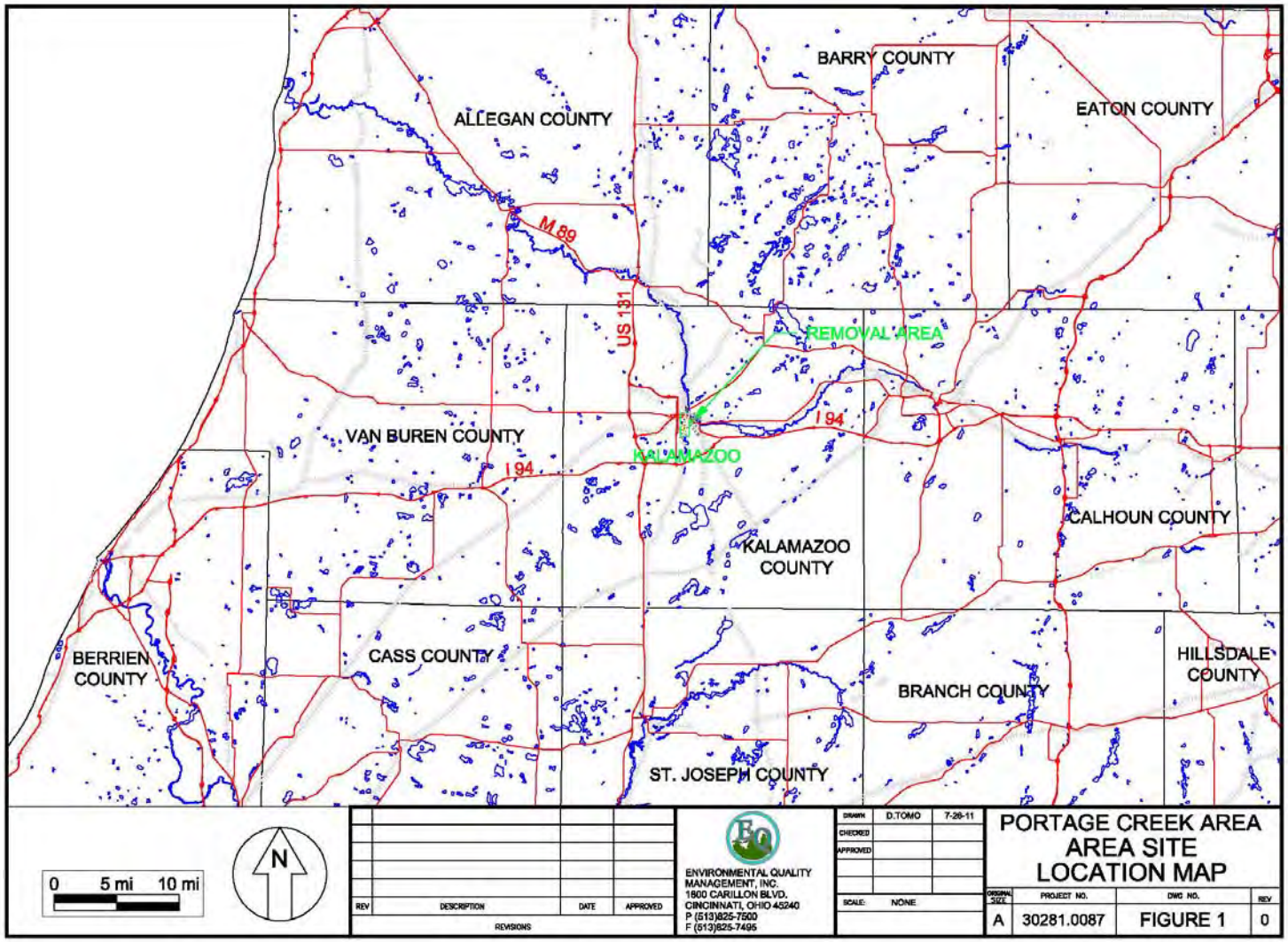

Figure 1. Site Location

3281-87PCA.1

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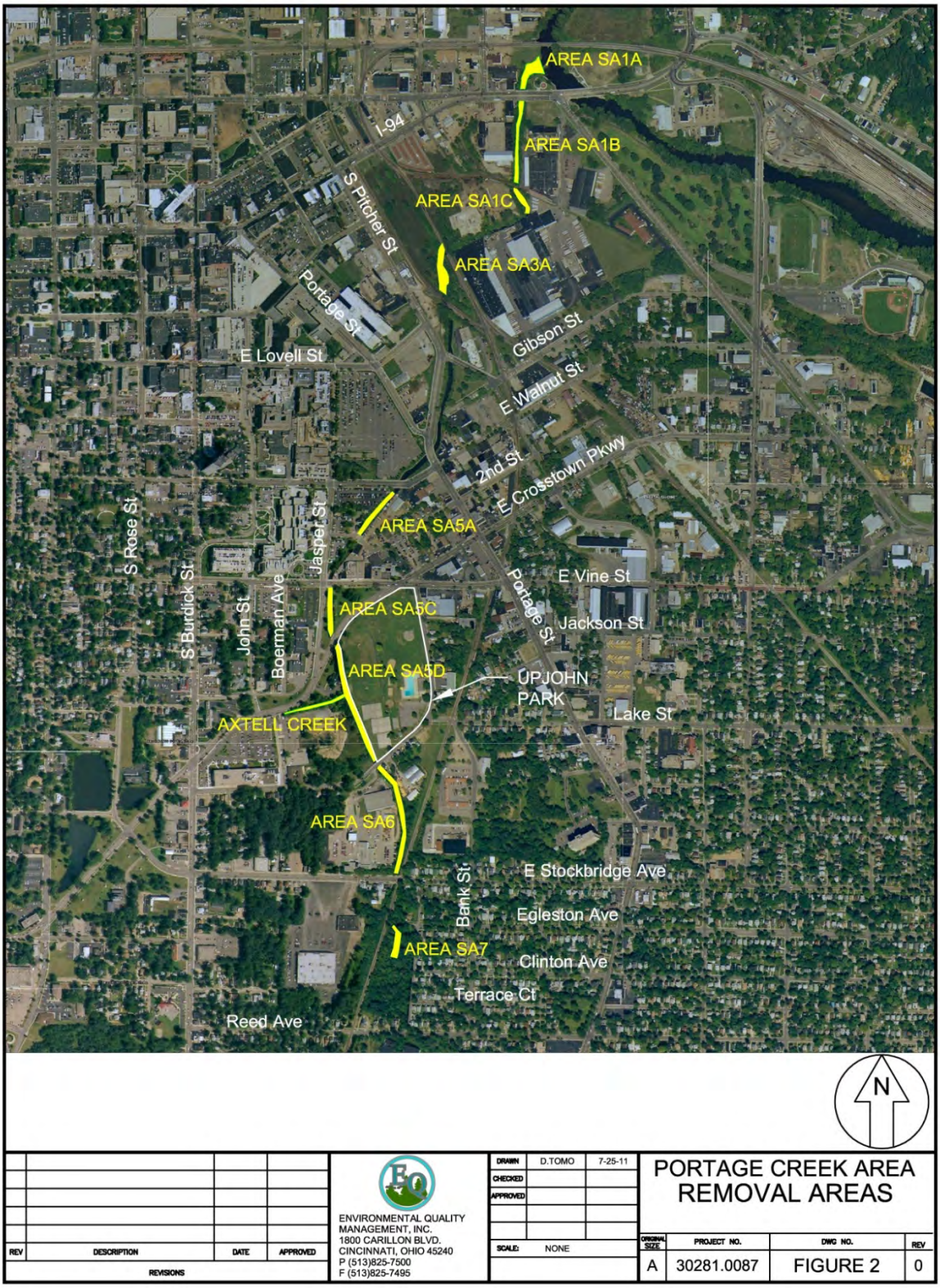

Figure 2. Removal Areas

3281-87PCA.1

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Figure 3. Removal Area SA7

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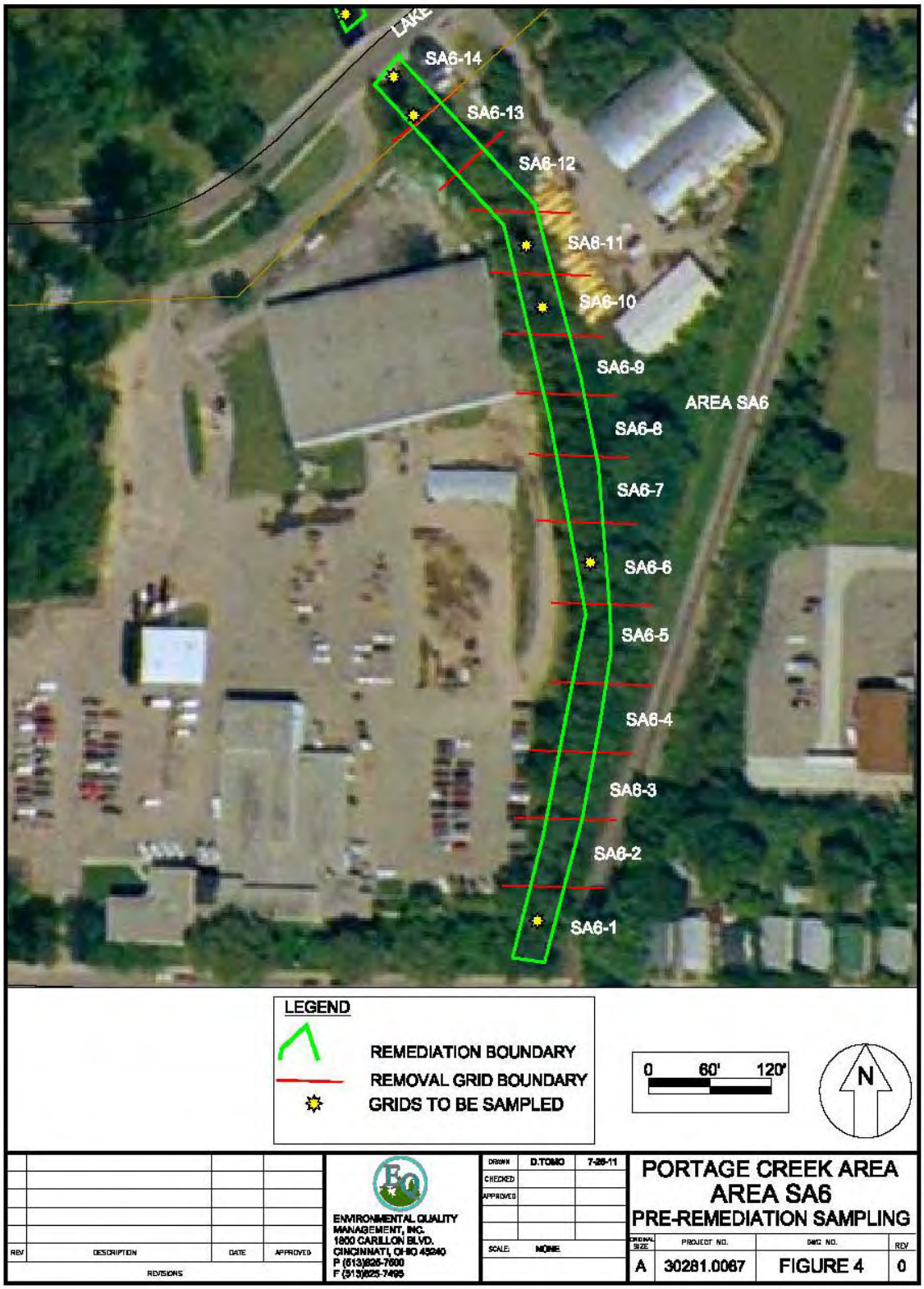

Figure 4. Removal Area SA6

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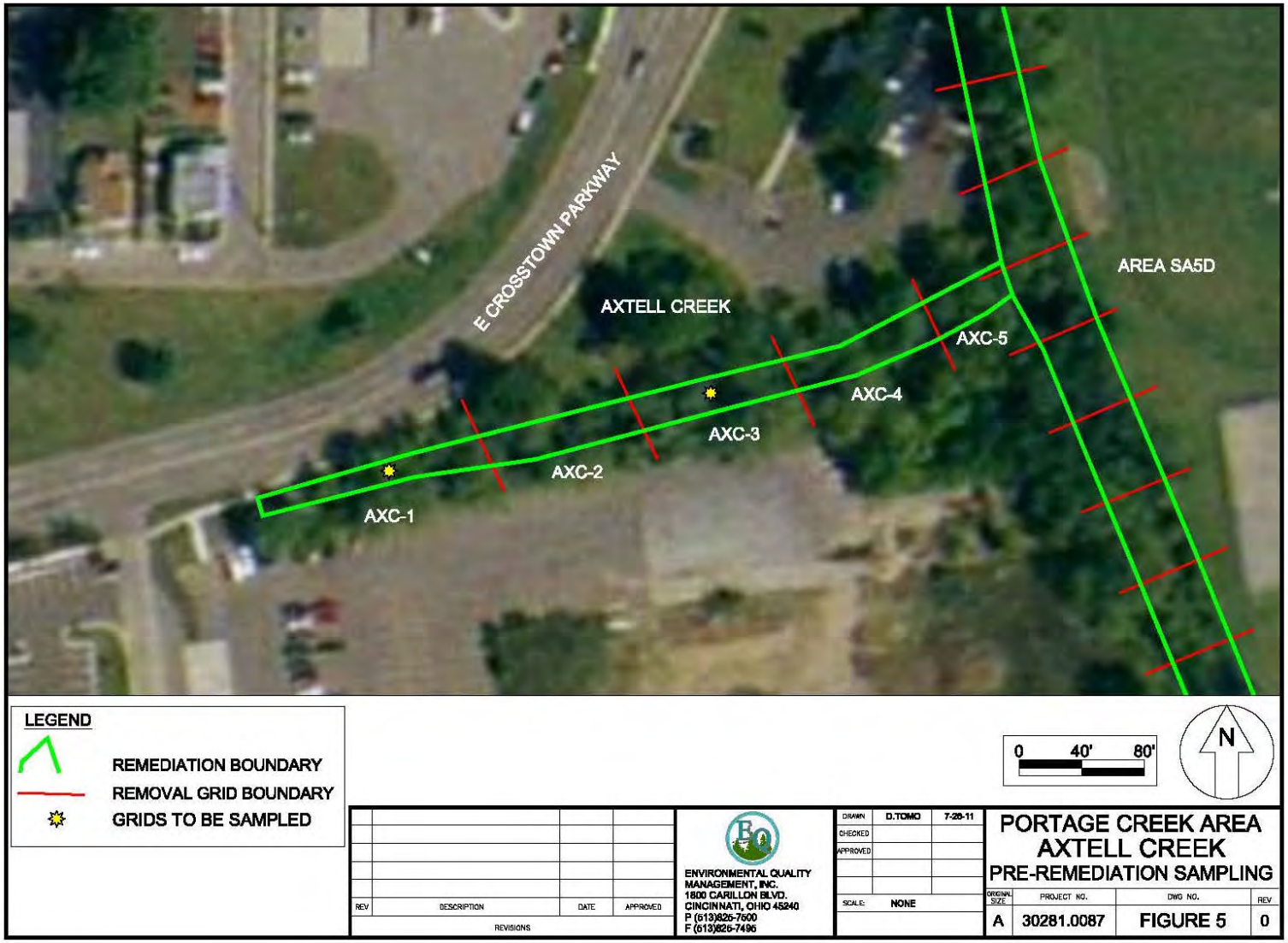

Figure 5. Removal Area Axtell Creek

3281-87PCA.1

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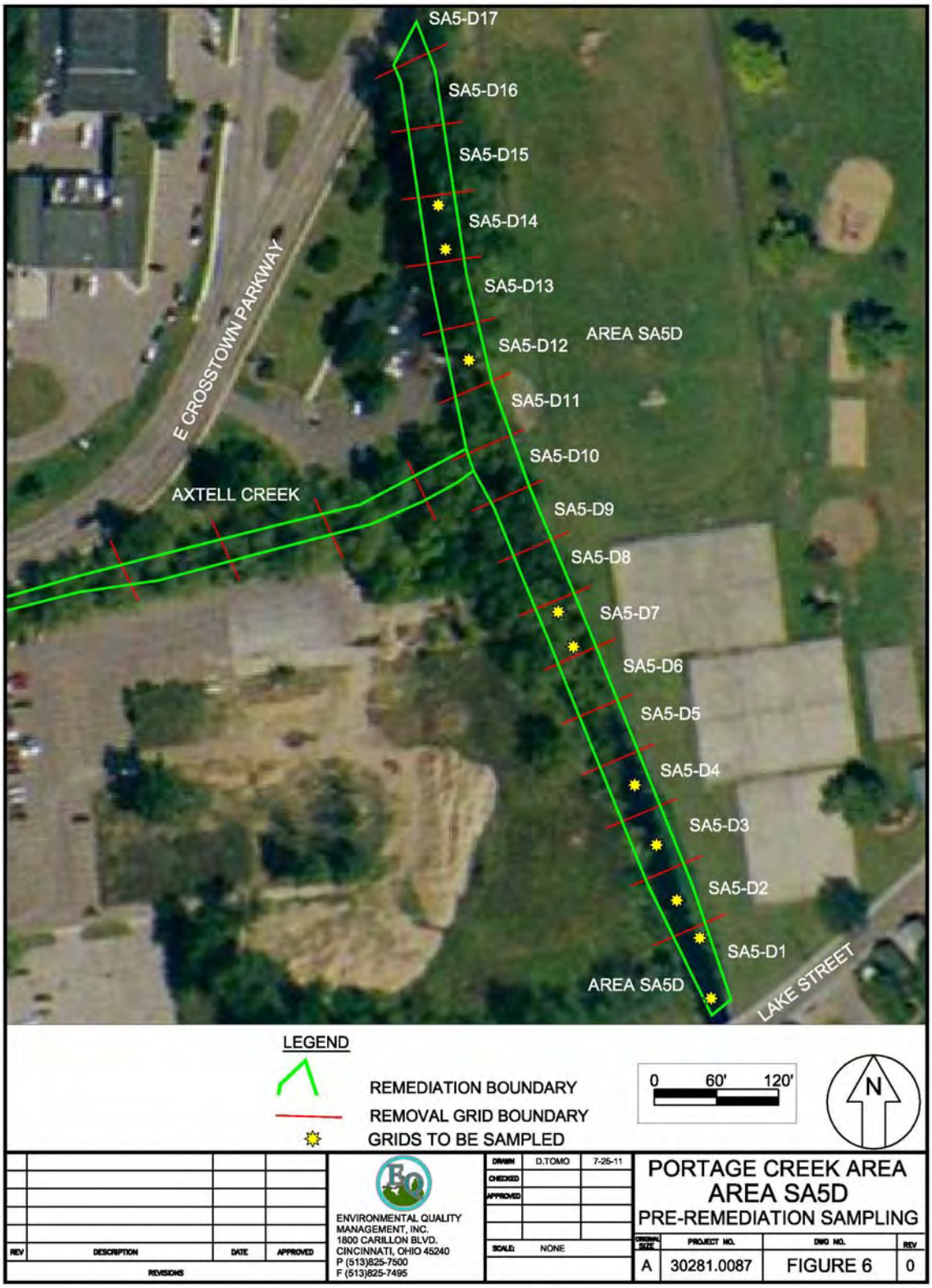

Figure 6. Removal Area SA5D

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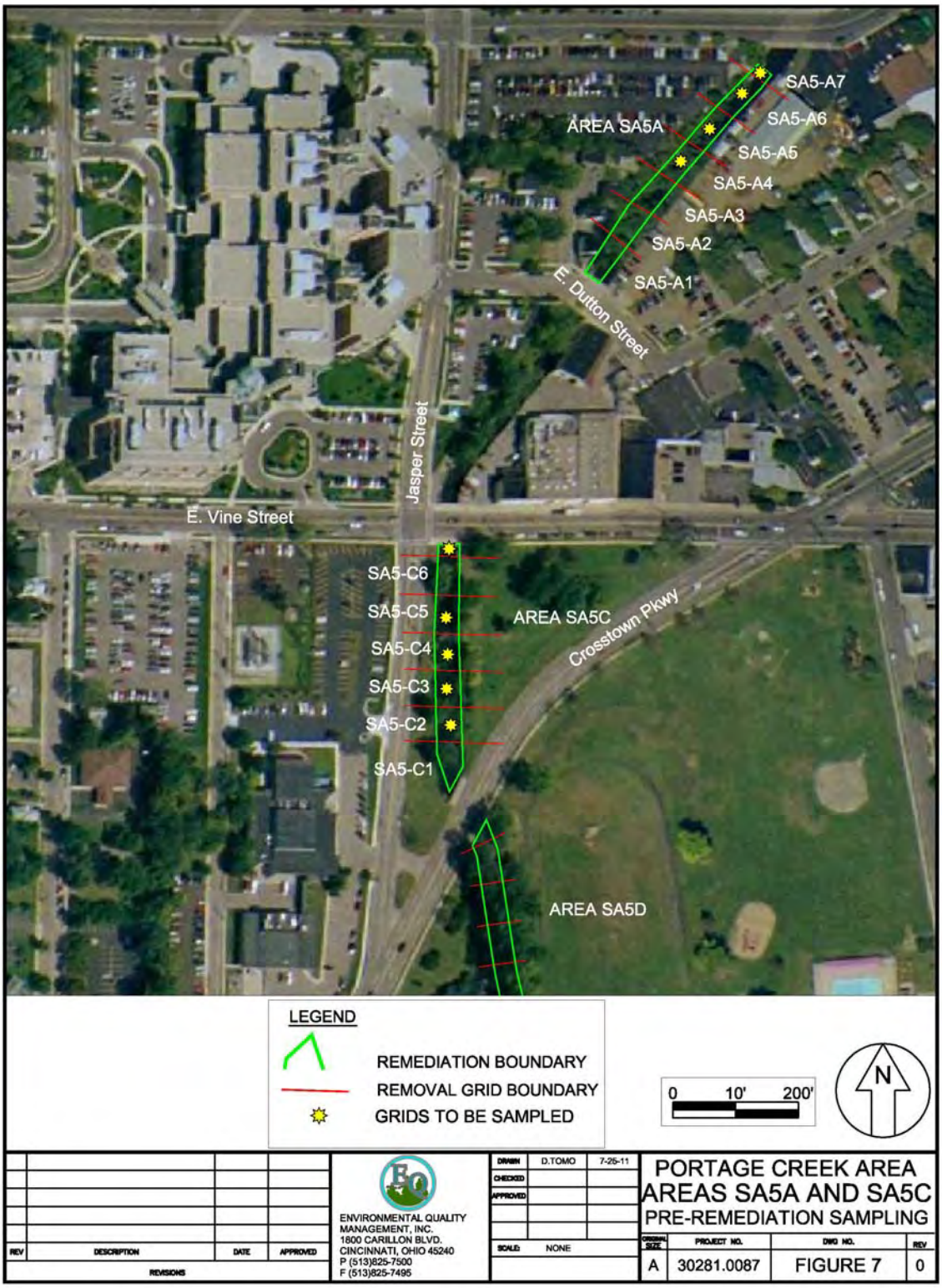

Figure 7. Removal Areas SA5A and SA5C

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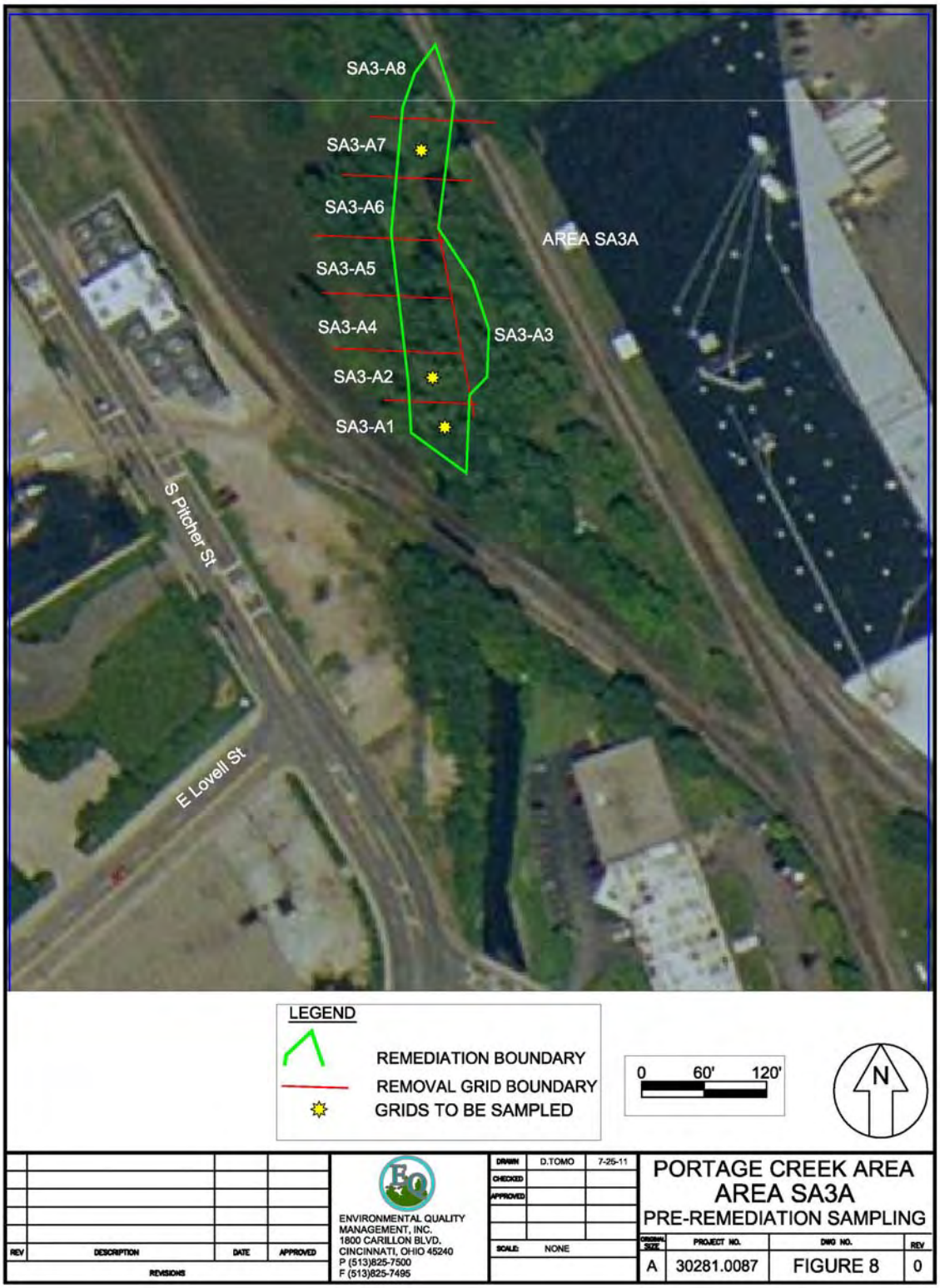

Figure 8. Removal Area SA3

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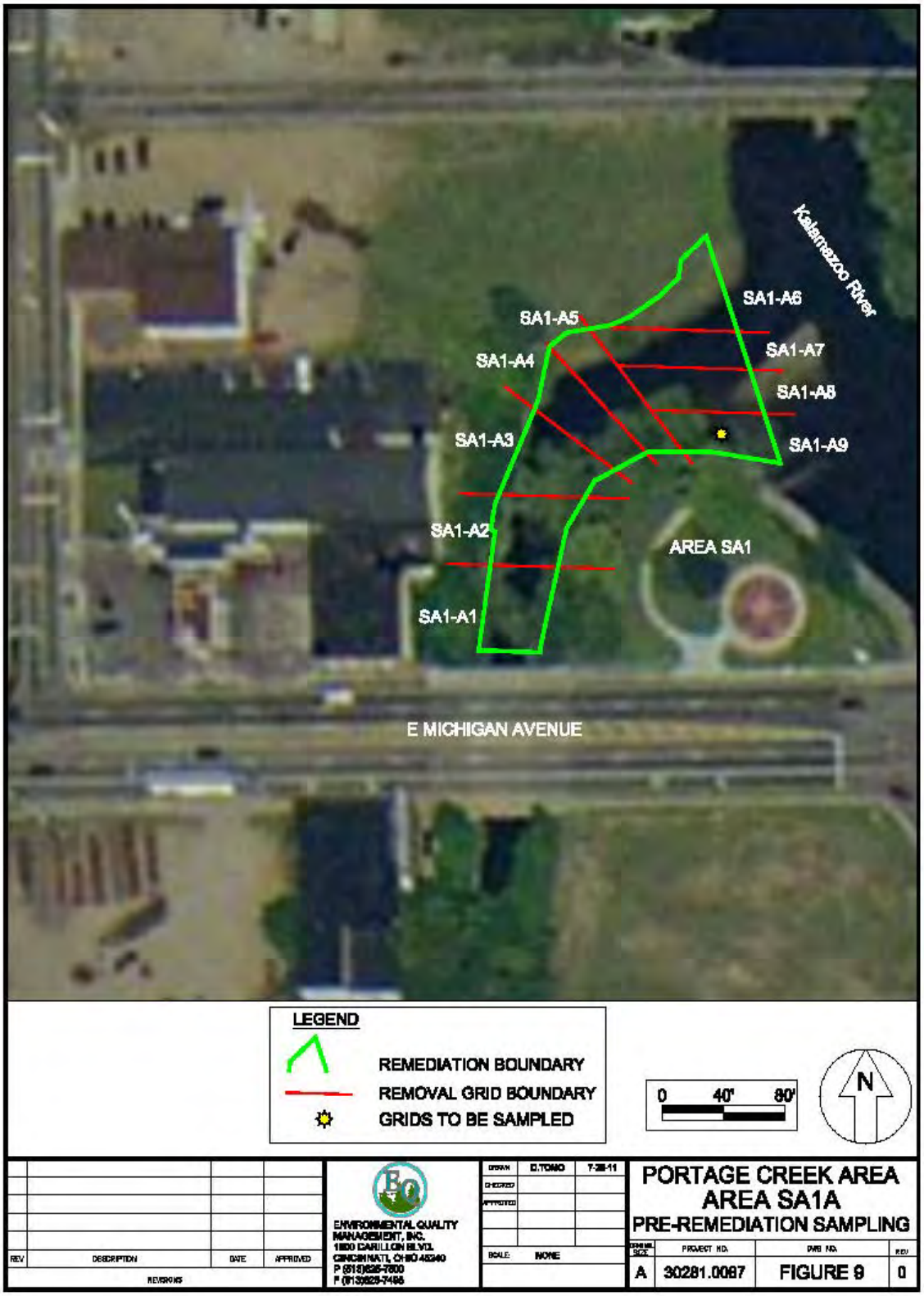

Figure 9. Removal Area SA1

3281-87PCA.1

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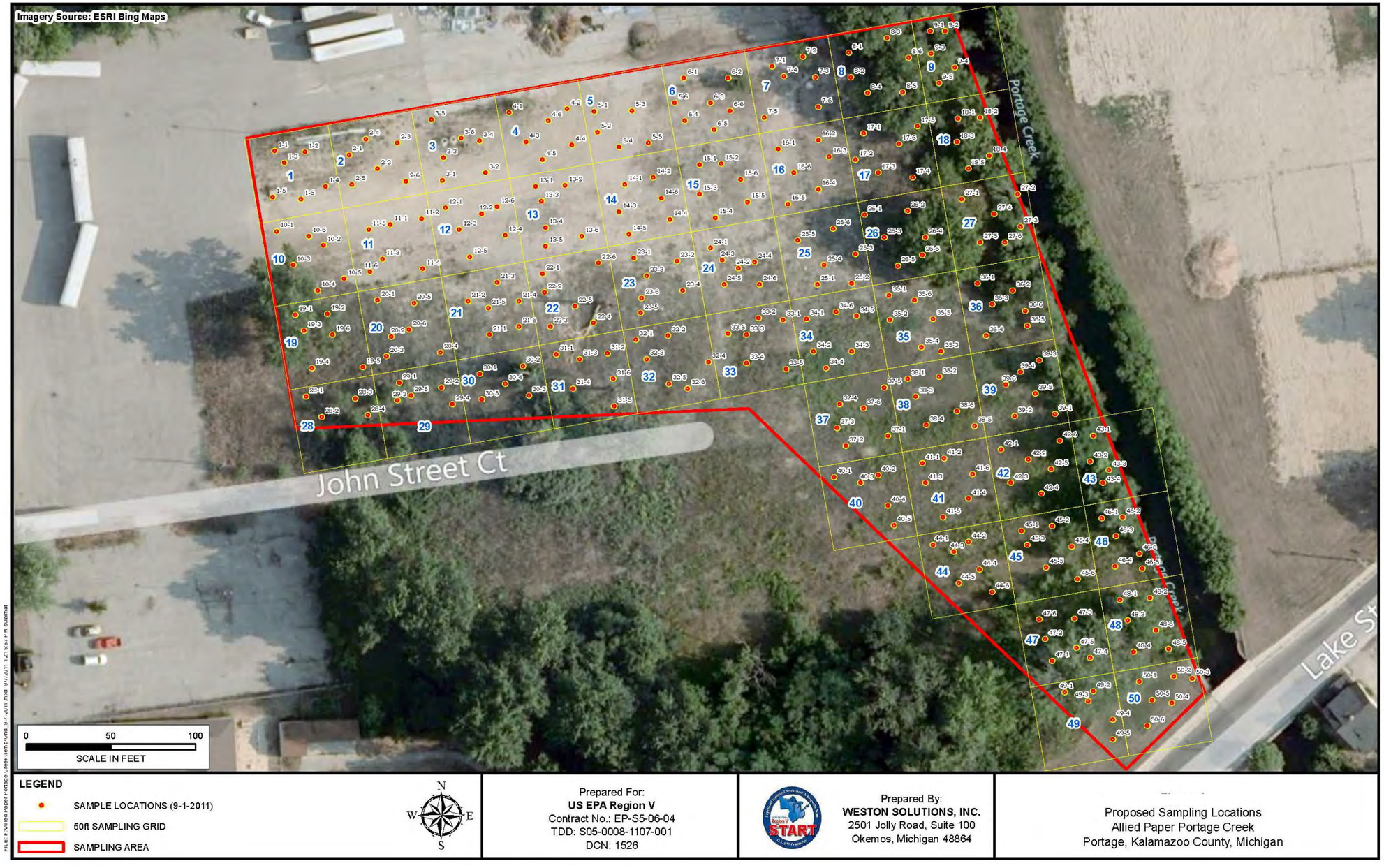

Figure 10. Sampling Locations at the Main Support Area

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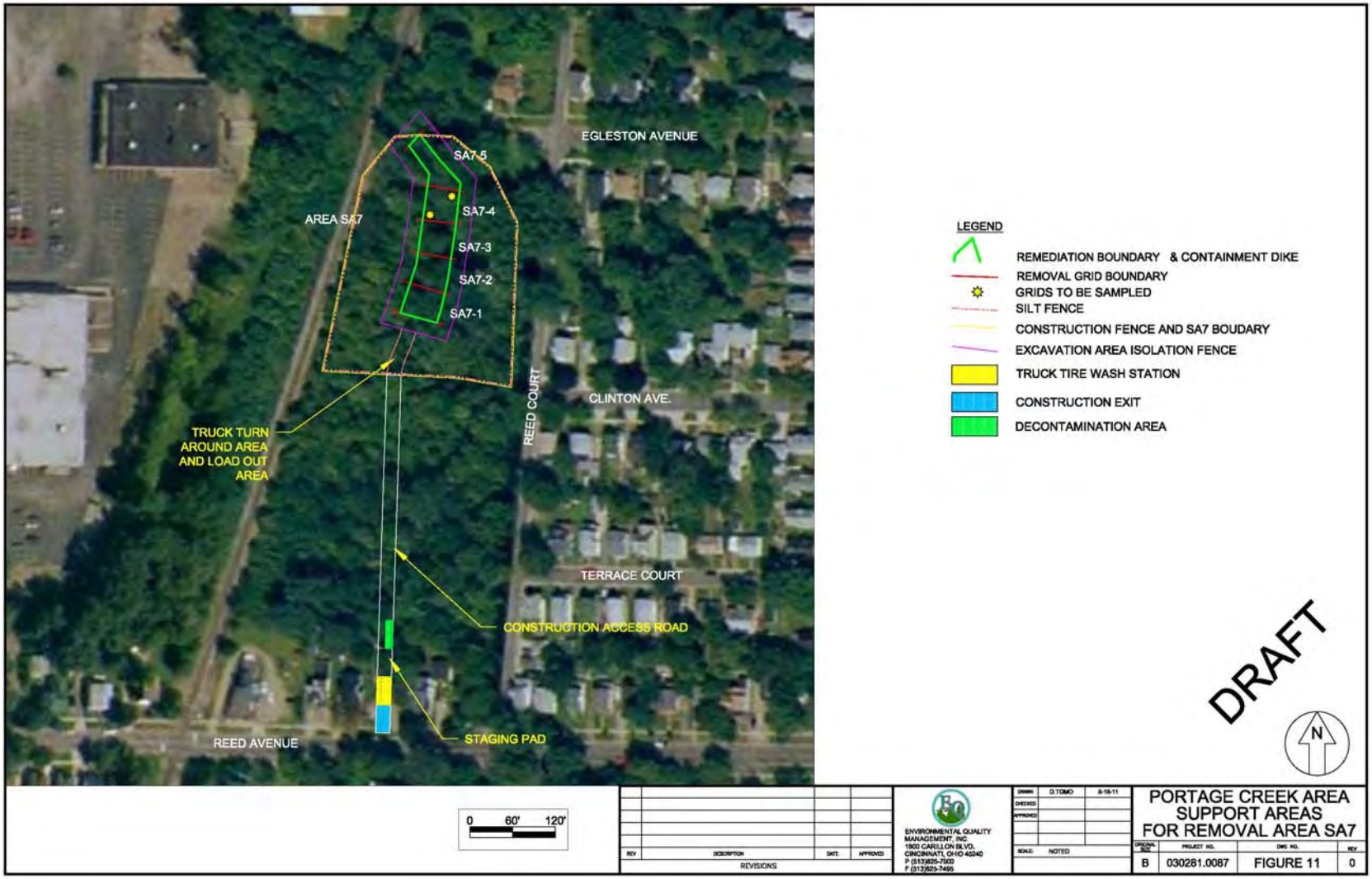

Figure 11. Support Areas for Removal Area SA7

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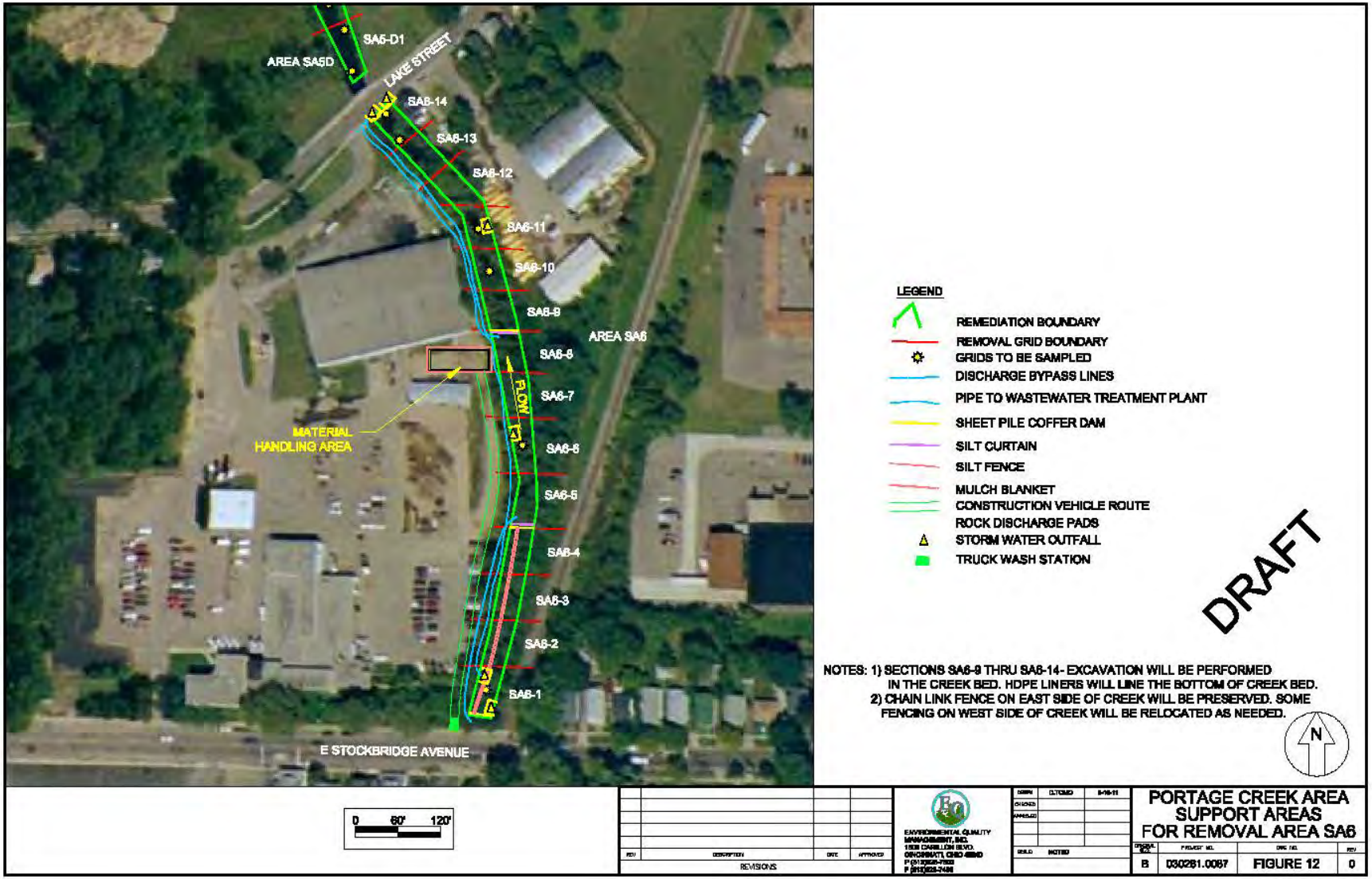

Figure 12. Support Areas for Removal Area SA6

3281-87PCA.1

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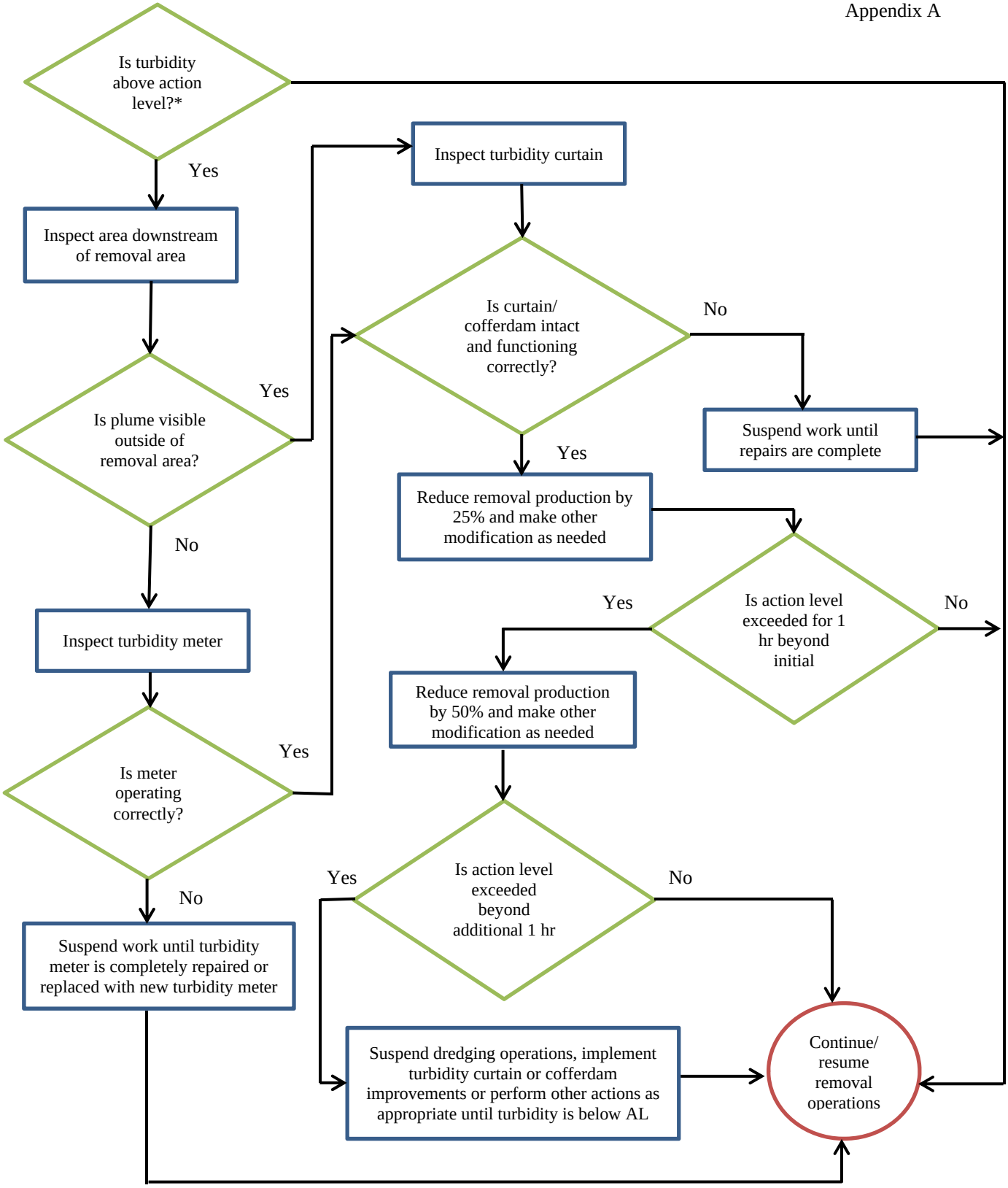

Figure 13. Mitigation Measures Flow Chart for Turbidity Monitoring

3281-87PCA.1

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EQ Environmental Quality Management, Inc.	BORING LOG	Boring No:

Site: _____
Location: _____
EQ Project No.: _____

Site Sketch/Diagram:

Drilling Contractor: _____
Driller: _____
Date(s) Drilled: _____
Drilling Method: _____
Borehole Diameter (in.): _____
Borehole Depth (ft.): _____
Logged by: _____
Air Monitoring Instrument: _____
Surface Elevation: _____
Depth to Water (ft.): _____
Well Installed (Y/N): _____

Comments:

Background = ppm

Depth (ft.)	Sample No.	% Recovery	Lithologic Description	Water @	Headspace (ppm)
0					

Page 1 of 1

Figure 14. Boring Log

3281-87PCA.1

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APPENDIX B

ANALYTICAL SOPs FOR TEST AMERICA LABORATORIES, INC.

This document was prepared by Environmental Quality Management, Inc. expressly for U.S. EPA. It shall not be released or disclosed in whole or in part without the express written permission of U.S. EPA.

Title: Flash Point in Liquids by Pensky-Martens Closed Cup Tester

US EPA Method 1010A, ASTM Method D93-06

Approvals (Signature/Date):

Ron Paulick — 7/30/10 Department Manager — Date	Jason Lykins — 7/30/10 EH&S Officer — Date
Violet Fanning — 7/30/10 Quality Assurance Manager — Date	Deborah Lowe — 7/30/10 Laboratory Director — Date

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1.0 Scope and Application

1.1 Flash point measures the response of the sample to heat and flame under controlled laboratory conditions. It is only one of a number of properties that must be considered in assessing the overall flammability hazard of a material. Flash point is used in shipping and safety regulations to define flammable and combustible materials. Flash point is also used to determine waste classification and disposal requirements.

1.2 This procedure is applicable for flash points in the range of ambient temperature to 110°C (230°F).

1.3 Flash point can indicate the possible presence of highly volatile and flammable materials in a relatively nonvolatile or nonflammable material.

1.4 Current default reporting limits are in the Laboratory Information Management System (LIMS).

1.5 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis as indicated in the Quality Assurance Manual.

2.0 Summary of Method

2.1 This method uses the Pensky-Martens closed-cup tester to determine the flash point of liquids. Liquids containing non-filterable, suspended solids also may be tested using this method.

2.2 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 source flame results in instant propagation of the flame in the vapor space above the sample.

3.0 Definitions

3.1 Flash point is the lowest temperature at which a combustible liquid evolves sufficient vapor, under the conditions of the test, to form a flammable vapor-air mixture that will flash when ignited.

3.2 Flammable is defined as a material that has a flash point less than 38˚C (100˚F).

3.3 Combustible is defined as a material that has a flash point greater than 38˚C (100˚F) but less than 93˚C (200˚F).

- Class I Combustible is defined as a material that has a flash point greater than 38˚C (100˚F) but less than 60˚C (140˚F).
- Class II Combustible is defined as a material that has a flash point greater than 60˚C (140˚F) but less than 93˚C (200˚F).

3.4 Please see the Glossary in the Quality Assurance Manual, DT-QAM-001, for additional definitions.

4.0 Interferences

4.1 Sample homogeneity and drafts can affect flash point values.

4.2 Erroneously high flash points may be obtained if precautions are not taken to avoid the loss of volatile material. Do not open containers unnecessarily. It is advisable to have a sample bottle dedicated to this analysis.

4.3 Do not store samples in plastic containers, since volatile material may diffuse through the walls of the enclosure.

4.4 Meticulous attention to all details relating to the flame exposure device, size of test flame, rate of temperature increase, and rate of dipping the flame exposure device into the vapor of the sample is necessary for good results.

4.5 Obtaining and analyzing a representative sample is of utmost importance. A sample may contain many constituents, having varying densities and flash points. Layers may form within the sample container and if the sample is not shaken prior to analysis, the potential of a more volatile layer being decanted and analyzed may occur, resulting in poor reproducibility.

4.6 Water vapors may evolve from liquid samples containing aqueous media, which may extinguish the test flame. If this occurs, continue to relight the flame and attempt flash point determination until the sample has reached a temperature of 93°C.

4.7 If the flame is extinguished when introducing the flame into the cup, quickly return the flame to its resting position to avoid introducing propane into the cup and causing a false flash. This is especially true when the flame turns from yellow to blue as it is introduced as this indicates that volatile vapors are present.

4.8 When a liquid contains flammable and nonflammable components, there are cases where this liquid can evolve flammable vapors under certain conditions and yet will not exhibit a close-cup flash point. This phenomenon is noted when a nonflammable component is sufficiently volatile and present in sufficient quantity to inert the vapor space of the closed cup, thus preventing a flash.

4.9 Some solid or viscous samples may liquefy when heat is applied. If this occurs, please make a note in the logbook and notify the Department Manager.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) 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

5.1.1 Analyst should exercise the appropriate safety precautions when setting and using the flame as the ignition source so as not to burn oneself. In addition, the temperature of the tester will reach temperatures above 110°C.

5.1.2 The analyst should exercise the appropriate safety precautions during the initial application of the ignition source, since test specimens containing low-flash material can give an abnormally strong flash when the ignition source is first applied.

5.1.3 In the event a sample ignites in the test apparatus do not attempt to remove the sample. Turn off the apparatus and flame. The flame should go out when the cup is closed. If this does not happen the flame may be extinguished by covering the sample with a non-flammable material or use of Halon fire extinguisher. After the apparatus has cooled the sample may be removed.

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	Hazards	Exposure Limit[1]	Signs and symptoms of exposure
Propane	Flammable	1000 ppm - PEL	Flammable liquid and gas under pressure. May cause frostbite to exposed skin. May cause dizziness and drowsiness.
Acetone	Flammable	1000 ppm - TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methylene Chloride	Flammable Carcinogen Irritant	25 ppm - TWA 125 ppm - STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Toluene	Flammable Poison	200 ppm – TWA	Very flammable liquid, flash point 7˚C. Harmful or fatal is swallowed. Harmful if inhaled or absorbed through skin and will cause irritation. May affect liver, kidneys, blood system or central nervous system.
p-Xylene	Flammable Irritant	100 ppm - TWA	Inhalation of vapors may be irritating to the nose and throat. Inhalation of high concentrations may result in nausea, vomiting, headache, ringing in the ears, and severe breathing difficulties, which may be delayed in onset. High vapor concentrations are anesthetic and central nervous system depressants. Skin contact results in loss of natural oils and often results in a characteristic dermatitis. May be absorbed through the skin. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.

[1] Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met

6.2 Pensky-Martens Closed-Cup Flash Tester.

6.3 ASTM Thermometer (-5° to +110°C): This mercury thermometer is used for tests in which the indicated reading falls within the limits 10° to +110°C. Alternatively, an electronic temperature measuring device, such as resistance thermometers or thermocouples, exhibiting the same temperature response as a mercury thermometer can be used.

6.4 Propane Fuel.

6.5 Halon fire extinguisher, mounted across from the ventilated work station.

6.6 Barometer with an accuracy of $\pm$ 0.15 in. Hg (0.5 kPa).

7.0 Reagents and Standards

7.1 The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

7.2 n-Decane: 99% purity or higher, purchased. May be used up through the expiration date provided by the vendor.

7.3 p-Xylene: Purchased from vendor.

- 7.3.1 p-Xylene is not suitable for high-temperature range Pensky-Martens Close-Cup Testing.
- 7.3.2 p-Xylene is stored at room temperature, in a flammable cabinet, up to 5 years from date opened.
- 7.3.3 The standard material can be reused. If this material does not meet the calibration target of 27.2 $\pm$ 2°C, fresh p-Xylene should be used.

7.4 Cleaning Solvents are suitable solvents that are capable of cleaning out the specimen from the test cup and drying the test cup and cover.

- 7.4.1 Acetone: purchased from vendor.
- 7.4.2 Toluene: purchased from vendor.
- 7.4.3 Methylene Chloride: purchased from vendor.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Liquid	Glass with air-tight lids	250 mL	Cool, <6.0°C	NA	NA

8.2 Successive test specimens can be taken from the sample container; however, the results of the flash point determination can be affected if the sample volume is less than 50% of the sample container for replicate analyses. Ideally, the headspace in the sample container should be between 15 and 50% when pouring up samples. The volume collected should be sufficient to ensure a representative sample, allow for duplicate analysis, and minimize waste disposal.

8.3 Do not open containers unnecessarily, to prevent loss of volatile material.

9.0 Quality Control

9.1 The following quality control samples are analyzed with each batch of samples:

Quality Controls	Frequency	Control Limit
Laboratory Control Sample (LCS)	1 per analytical batch	27.2 ± 2°C
Duplicate (DUP)	1 per each sample that flashes.	± 3°C *

* Due to system limitations, the Duplicate Control Limit is not monitored through the LIMs.

9.2 Perform the following calibrations on an annual basis.

9.2.1 All annual calibration information is recorded in the instrument maintenance log. The instrument is tagged with the calibration expiration date (one year from the calibration date).

9.2.2 Verify the stirrer rotations. The rotation should be 90-120 rotations per minute.

9.2.3 Verify the rate of increase of the temperature. The temperature should increase at a rate of 1 - 5°C per minute.

9.2.4 Analyze an n-Decane standard, acceptance criteria is 52.8 ± 2.3°C (50.5 – 55.1°C). Record this information in the instrument maintenance log.

9.3 Laboratory Control Standard (LCS)

9.3.1 The LCS is a p-Xylene standard that is subjected to the same conditions that a sample undergoes. The LCS verifies that the analytical system is in control.

9.3.2 The LCS is analyzed at the beginning of each analytical batch.

9.3.3 The recovery of the LCS must be within 2°C of the true flash point of the p-Xylene standard, which is 27.2°C.

9.4 Duplicate (DUP)

9.4.1 A DUP is performed for each sample that flashes.

9.4.2 If the DUP does not confirm a sample flash within ± 3°C, the sample is tested a third time.

9.5 All QC and sample results are recorded in the Flash Point Spreadsheet.

9.6 Liquid in glass thermometers are checked once a year against an NIST standard thermometer.

10.0 Procedure

10.1 The analysis takes place with the apparatus set up in a ventilated work station (VWS). VWS has a reduce draw compared to fume hoods and has a minimal interference of draft across the test cup.

10.2 Instrument Calibration

10.2.1 Determine the flash point of the LCS (p-xylene) at the beginning of the run. A value of 27.2 ± 2˚C must be obtained for the LCS to be considered acceptable.

10.2.2 If the LCS fails, pour a fresh portion of p-Xylene and check the condition and operation of the apparatus, especially with regard to the tightness of the lid, the action of the shutter, and the position of the test flame. After adjustment, repeat the LCS analysis. The LCS may be repeated once. If it still fails, corrective action must be taken.

10.3 Sample Analysis

10.3.1 Thoroughly clean and dry all parts of the cup and its accessories before starting the test, being sure to remove any solvent which had been used to clean the apparatus. The cup can be cleaned with a suitable solvent, such as acetone, toluene, or methylene choride. followed by soapy water to remove any traces of residue remaining from a previous test. If any traces of carbon or other material are present, rub with steel wool until the surface is shiny. Flush the cup with cold water and thoroughly dry with a paper towel.

10.3.2 Record the barometric pressure in the Flash Point spreadsheet.

10.3.3 Thoroughly mix the sample to be tested by inverting the sample container. Fill the cup with the sample to the level indicated inside the cup.

10.3.4 The sample temperature to be tested should be less than 25°C. Samples with low flash points should be kept chilled to prevent accidental flash when the ignition source is applied at 25°C.

10.3.5 Set the cup in the heating unit. Place the lid on the cup making sure the locking device is properly engaged. Support the thermometer with the bulb ¼” from the bottom of the cup and located at a point halfway between the center and side of the cup on a diameter perpendicular to the line of the sweep of the test flame and on the side opposite to the test flame burner arm.

10.3.6 Connect the stirrer to the stirrer motor and turn the switch on. Turn the stirrer 90 to 120 rpm, stirring in a downward direction.

10.3.7 Light the test flame and adjust it to 5/32 in (4 mm, about the size of the tip on a lead pencil) by adjusting the knob on the propane cylinder.

10.3.8 Adjust the supply of heat by adjusting the dial on the powerstat until the temperature reading on the thermometer increases by 1 - 5°C (2 - 10°F) per minute.

10.3.9 Apply the test flame at 25°C and at temperature readings of at least 2°C increments. Apply the test flame by operating the knurled hand knob controlling the shutter and test flame burner, so that the flame is lowered into the vapor space of the cup in 0.5 second, left in its lowered position for 1.0 second, and

quickly raise to its high position. Do not stir the sample while applying the test flame.

Note: If the flame turns from yellow to blue when being introduced into the cup and extinguishes itself, the vapors may be such that the flame may have to set in the opening for 5 seconds rather than in the cup for 1 second to obtain the flash point.

10.3.10 Record the temperature reading on the thermometer at the time a distinct flash in the interior of the cup is observed. The sample is deemed to have flashed when upon application of the test flame a large flame appears and instantaneously propagates itself over the entire surface of the test specimen. The characteristics of a distinct flash are a quick blue or white light inside the cup that should cause flames to rise out of the three openings in the lid. The flame turning from yellow to blue is an indication that a sample may flash. A bluish halo may surround the test flame at applications preceding the actual flash.

10.3.11 Certain mixtures containing halogenated hydrocarbons, such as methylene chloride or trichloroethylene, do not show a distinct flash as defined in 10.3.10. Instead a significant enlargement of the test flame from yellow-blue to yellowish-orange or yellowish-green occurs depending upon the halide.

10.3.12 If the sample boils at 93° - 104°C, and repeated introductions (three) of the flame result in the flame being immediately extinguished each time, discontinue analysis and report sample as having a flash point >100°C. Alternately, report sample as “non-ignitable @ 100°C.” NOTE: the boiling point of water is 100°C.

10.3.13 If the sample does flash, report result to nearest 0.5^{o}C or 1°F and repeat the test following Section 10.4.

10.4 Duplicate Flash Point Analysis

10.4.1 Empty tester cup and clean the flash residue from it. Fill the tester cup to the level indicated inside the cup with a well-mixed, fresh sample.

10.4.2 Set the tester up in accordance with 10.3.5 through 10.3.8.

10.4.3 Based on the previously observed flash point, heat sample until it reaches a temperature that is 23 ± 5°C below the expected flash point. At this point, the temperature rate of increase should be 1 to 2°C per minute. Apply the test flame at this temperature and every 1°C until the sample flashes again.

10.4.4 If the initial flash recorded was less than 18°C of the initial application of the ignition source, chill the sample, if possible, until its temperature is 25°C below its observed flash point. Begin the test at this point by applying the ignition source when the temperature is 23 ± 5°C below the expected flash point and every 1°C until the sample flashes again.

Note: For samples that flash at room temperature, this requirement cannot be met. Chill sample to as low as possible and conduct the test.

10.4.5 The duplicate results should be within 3°C. If results do not agree within the specified range, then repeat the analysis again.

11.0 Calculations / Data Reduction

Results are all determined using a Celsius thermometer. Values are converted to Fahrenheit as required to meet client needs.

11.1 Conversion from Celsius to Fahrenheit

$$^{o}F = (9/5) \times {}^{o}C + 32$$

11.2 Conversion from Fahrenheit to Celsius

$$^{o}C = ({}^{o}F - 32) \times (5/9)$$

11.3 Barometric Pressure (BP) Conversion from inches Hg to mm Hg

$$\text{BP in mm Hg} = \text{BP in. Hg} \times 25.4$$

11.4 °F Correction for Barometric pressure

Corrected Flash point (CF) = $^{o}F + 0.06\ (760 - BP)$

Where: ^{o}F = observed flash point in Fahrenheit
BP = BP in mm Hg from equation 11.3

11.5 °C Correction for Barometric pressure:

Corrected Flash point (CF) = $^{o}C + 0.033\ (760 - BP)$

Where: ^{o}C = observed flash point in Celsius
BP = BP in mm Hg from equation 11.3

11.6 Relative Percent Difference (RPD)

$$RPD = \frac{|C_1 - C_2|}{(C_1 + C_2/2)} \times 100\%$$

Where: C_1 = Measured Flash Point of Sample
C_2 = Measured Flash Point of Duplicate

12.0 Method Performance

The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.1 Demonstration of Capabilities - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.2 Method Detection Limit Study - Are not performed for this procedure.

12.3 Training Requirements – Training requirements and documentation are described in the TestAmerica Dayton QA Manual (DT-QAM-001).

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.2 The following waste streams are produced when this method is carried out.

- Excess non-flammable samples are disposed of in the trash.
- Excess flammable samples and waste solvents are disposed of in the flammable waste drum in the hood.
- Waste solvents are disposed of in the flammable waste drum.

15.0 References / Cross-References

15.1 American Society for Testing and Materials, ASTM D93-06, Test Methods for Flash Point by Pensky-Martens Closed Cup Tester.

15.2 Electric Pensky-Martens Tester, Instructions for Use.

15.3 Test Methods for Evaluating Solid Waste, SW 846, 3rd Edition, Method 1010A, Test Methods for Flash Point by Pensky-Martens Closed Cup Tester.

15.4 DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton.

15.5 TestAmerica Company Wide Environmental Health and Safety Manual, CW-E-M-001.

15.6 DT-QA-005 Procedure for Balance Calibration Check

15.7 DT-QA-006 Thermometer Calibration

16.0 Method Modifications

Item	Method	Modification
	1010	References ASTMD-93-79 & 80, our Laboratory is referencing ASTMD-93-06
	ASTM 93	The method is applied from ambient room temperature or 25˚C to 110˚C instead of 40˚C to 110˚C.
	ASTM 93	Follow stirring recommendation of Procedure A for SOP. Instrument not capable of attaining 250 rpm as specified in Procedure B.
10.3	ASTM 93	Analytical technique modified to allow quicker determinations of unknown flash points. If sample flashes, a duplicate is then performed following the more restrictive guidelines.

17.0 Attachments

None

18.0 Revision History

18.1 Revision Dates

- 7/30/2010 Biennial update
- 7/22/2008 Original (replaces DT05-19.3)

18.2 Changes from last revision

Section	Change from	Change to	Reason
3.0	NA	Add additional definitions.	Consistency with method nomenclature.
4.7	NA	Added potential interference from propane gas if flame is extinguished within the cup.	Consistency with method instructions.
5.2	NA	Added propane and toluene to the hazard table.	Consistent with laboratory practices.
6.3	NA	Added electronic temperature measuring device.	Consistency with method instructions.
6.5	NA	Halon fire extinguisher	Consistent with laboratory practices.
7.4	NA	Added acetone, toluene and methylene chloride as cleaning solvents.	Consistency with method instructions and laboratory practices.
9.1 9.3.3 9.4.2	DUP statistical limits DUP every ten or every flash.	DUP ± 3˚C DUP every flash.	Consistency with method instructions.
10.1	Turn fume hood off or use draft shield.	Use ventilated work station.	Consistent with laboratory practices.
10.3.9	Apply test flame in multiples of 2˚C.	Apply test flame at least every 2˚C.	Consistent with laboratory practices.

Section	Change from	Change to	Reason
10.3.9	NA	Added Note regarding the application of the flame in the cup opening for 5 seconds if flame turns blue and extinguishes itself.	Consistent with laboratory practices.
10.4.3 10.4.4	Insert flame beginning 23˚C below the flash point.	Insert flame beginning at 23± 5˚C.	Consistency with method instructions.
10.4.4	NA	Added Note regarding chilling samples that flash at room temperatures.	Consistent with laboratory practices and clarity to method instructions.
13 & 14	Section 13 – Waste Management and Pollution Control	Section 13 separated into two sections: Section 13 – Pollution Control and Section 14 – Waste Management	Compliant with new SOP format recommendations.
15	NA	Added SOPs DT-QA-005, DT-QA-006	Compliance with SOP requirements.
16 & 17	NA	Switched order	Consistency with other SOPs.

Title: pH
EPA 150.1, SM 4500 H^+B, SW846 9040C & 9045D

Approvals (Signature/Date):

3/25/10 Ron Paulick Date Department Manager	3/26/10 Jason Lykins Date EH&S Officer
3/25/10 Violet Fanning Date Quality Assurance Manager	3/26/10 Deborah Lowe Date Laboratory Director

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1.0 Scope and Application

1.1 This procedure is applicable to drinking, surface, ground water, domestic and industrial waters and soils. Different preparation and analytical techniques are used depending upon the applicable method and composition of the sample.

1.2 Reporting Limits are not applicable to this test. For purposes of Electronic Data submittals an RL may be assigned. Typically this is set at 0.1 pH unit.

1.3 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis as indicated in the QA Manual.

2.0 Summary of Method

There are several procedures described in this SOP. The composition of the sample determines the procedure followed.

2.1 For drinking water or aqueous samples, the pH can be determined electrochemically by electrode combined with automatic temperature compensation according to EPA 150.1 or SM 4500 H^+B. EPA 150.1 is not currently an approved test method for NPDES.

2.2 If the sample has an aqueous phase that constitutes at least 20% of the total volume of the sample, the pH can be determined electrochemically by electrode combined with automatic temperature compensation according to SW846 9040C.

2.3 If the sample does not have an aqueous phase of at least 20% of the total volume of the sample, the sample is first mixed with reagent water and the pH measured electrochemically by electrode combined with automatic temperature compensation according to SW846 9045D.

3.0 Definitions

3.1 pH is the measure of the activity of the hydrogen ion in a solution. The greater the activity, the more acidic the solution; the lesser the activity, the more basic the solution.

3.2 Samples with a pH of =7 are considered “neutral”.

3.3 Samples with a pH of <7 are considered “acidic”.

3.4 Samples with a pH of >7 are considered “basic”.

3.5 Batch - A group of environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours.

3.6 Replicate – separate aliquots of sample or leachate that are analyzed sequentially until the values differ by 0.1 SU or less.

4.0 Interferences

4.1 The glass electrode, in general is not subject to interferences from color, turbidity, colloidal matter oxidants, reductants, or high salinity.

4.2 Coatings, oily material or particulate matter on the electrode can impair response. Gentle wiping, detergent washing or soaking in dilute acid can remove these coatings. Please see the cleaning instructions provided by the electrode manufacturer for cleaning details.

4.3 The electrometric determination of pH is affected by temperature in two ways. The first is mechanical that are caused by the changes in the properties of the electrode at various

temperatures. This interference is partially overcome by the use of the automatic temperature compensation electrode. The second source of temperature effects is the change in the chemical equilibrium of the solution at various temperatures. As temperature increases, the hydrogen ion activity increases, thus lowering the pH due to changes in the sample temperature. This error is sample dependent and cannot be controlled. Therefore, the pH and temperature should be recorded at the time of the analysis. To minimize the overall affect of temperature on pH measurements, the samples should be analyzed at room temperature, the same temperature as the buffers used to calibrate the pH meter.

4.4 Although pH is due solely to hydrogen ion activity, samples with varying ionic species and ionic strengths will affect hydrogen ion activity.

4.5 Samples should be analyzed as soon as possible after receipt at the laboratory.

4.6 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.

4.7 If the sample is multiphasic, decant the oily phase and measure the pH of the aqueous phase.

4.8 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a low-sodium-error electrode. Glass electrodes can yield erroneously lower values at high temperatures and pH over 10. Conversely, glass electrodes can yield erroneously higher values at pH below 1.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), 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

Samples that have a very high or very low pH may cause burns if they come in contact with the skin.

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 standards 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
Hydrochloric Acid	Corrosive Poison	5 ppm - Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

- Magnetic stirrer with Teflon stir bar.
- Shaker table.
- Centrifuge.
- Miscellaneous glassware.
- Disposable plastic beakers.
- Filter paper, Whatman #4 or similar type.
- pH meter with automatic temperature compensation electrode. A backup electrode should be kept on hand. Sealed or epoxy probes are not acceptable due to OEPA requirements.
- Balance capable of weighing 0.1 grams.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents 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 questionable, analyze the reagent to determine the level of impurities.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

All standards/reagents are stored at room temperature.

7.1 **Distilled Water:** Prepare by passing through a reverse osmosis system followed by a mixed bed of cation and anion exchange resins.

7.2 **1:10 HCL Solution**: Prepare by adding 5 mL of concentrated HCL to 50 mL of DI water in a beaker. The solution is used to clean oily material off the electrode. It is also acceptable to wash with acetone or methanol. See the electrode instructions for additional cleaning information. Larger quantities can be prepared using the established ratio with a shelf life of 1 year.

7.3 **Buffer solutions:** Buffers having a pH of 2.00, 4.00, 7.00, 10.00 and 12.00 for calibrating the pH meter. In addition, a second source of one of the buffer solutions is needed for the use as the Initial Calibration Verification Standard. Shelf life: 6 months from the date opened or manufacturer's expiration date, whichever one comes first. Exposure to air affects the buffer shelf life so keep the container tightly closed when not in use.

7.4 **ICV Buffer Solution:** pH Buffer of 4.00 that is obtained from a different source than the one used to prepare the standard used to construct the curve. Shelf life: 6 months from the date opened or manufacturer's expiration date, whichever one comes first. Exposure to air affects the buffer shelf life so keep the container tightly closed when not in use.

7.5 **Buffer Solutions:** Buffers having a pH of 1 or 13 used to check pH response when the pH of samples are outside the calibration range. Shelf life: 6 months from the date opened or manufacturer's expiration date, whichever one comes first. Exposure to air affects the buffer shelf life so keep the container tightly closed when not in use.

7.6 **Electrolyte Solution:** manufacturer's internal filling solution for the pH probe.

7.7 **Methanol:** Solvent used to clean the probe as needed, especially for oily samples.

7.8 **Acetone:** Solvent used to clean the probe as needed, especially for oily samples.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	Plastic or glass	250 mL	Cool $\leq$ 6.0^{o}C	15 Minutes 24 Hours	150.1 / MUR 9040C / EPA MICE
Soil	Glass	4-oz.	Cool $\leq$ 6.0^{o}C	7 Days	9045D / EPA MICE

8.1 Aqueous samples should be collected with as little headspace as possible. Samples not at equilibrium with the atmosphere are subject to changes when exposed.

8.2 Methods 9040C, 9045D: Holding Time is listed as "As Soon as Possible" in SW 846. Per EPA MICE, the recommended maximum holding time for pH in water is 24 hours and pH in soil is 7 days. There are no mandated regulatory requirements.

8.3 For drinking water and NPDES, the hold time is listed as "As Soon as Possible," which is defined as within 15 minutes per the Method Update Rule.

8.4 For drinking water or NPDES compliance testing, the analysis must be performed in the field at the time of analysis. If transported to the laboratory for analysis, the analysis will be performed as soon as practical and reported qualified.

8.5 For Laboratory purposes, it is our intent to analyze all water pH samples with 24 hours.

9.0 Quality Control

9.1 The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Laboratory Control Sample (LCS)	1 per batch of 20 samples or less.	0.1 SU
Replicate	Every sample.	0.1 SU

9.2 Batch QC consists of:

9.2.1 Buffer solutions (2, 4, 7, 10, & 12) used for ICV, CCV, and LCS.

10.0 Procedure

10.1 Initial Calibration: Prepare a referenced calibration curve and Initial Calibration Verification (ICV) on a daily basis, whenever the CCV recovery is no longer acceptable, or if major instrument repairs are performed. Calibration is performed daily as a requirement of OEPA certification.

10.1.1 Calibration must include at a minimum the use of 2 Standard Buffers bracketing the pHs of the expected sample range and are approximately three pH units apart.

10.1.2 For methods EPA 150.1 and SM4500 H-B, typically a three point calibration is performed using pH buffers of 4, 7, and 10.

10.1.3 For methods SW9040C and SW9045D, typically a five point calibration is performed using pH buffers of 2, 4, 7, 10, and 12.

10.1.4 Place the pH probe and the ATC into a buffer. Allow the readings to stabilize and set the meter to the pH value listed for the buffer at the test temperature.

10.1.5 Repeat procedure with the remaining buffers.. Check and record the slope and temperature after calibration.

10.1.6 The correct value for the final slope is 59.1 mV/pH. The slope acceptance criteria is 95-105% (56.145 – 62.055 mV/pH) before analysis can proceed.

10.1.7 If slope is not within the acceptable range, the calibration may need to be preformed with fewer buffers or the probe may require cleaning or maintenance.

10.2 Initial Calibration Verification (ICV).

10.2.1 The purpose of the ICV is to verify that the calibration standard and instrument performance are acceptable. The ICV must be obtained from a different source than the one used to prepare the standard used to construct the curve.

10.2.2 The ICV is prepared and analyzed in the same manner as the calibration curve. The ICV must be analyzed immediately after the calibration curve. Acceptance criteria is ± 0.1 pH units of true value. Repeat calibration if the acceptance criteria are not met.

10.3 Continuing Calibration Verification Standard (CCV).

10.3.1 Analyze a standard buffer at the beginning of the batch, every 10 analyses, and at the end of the analytical run. The ICV may serve as the beginning CCV if samples are analyzed shortly after calibration.

10.3.2 The standard buffer used for CCV should be representative of the samples analyzed. A pH 4 buffer should be used for acidic samples and a pH 10 buffer should be used for basic samples. If samples are in the range of pH 6-8, then a pH 7 buffer should be used. Any of the CCVs may be used as the batch LCS. Identify the LCS/CCV with the batch number.

10.3.3 Acceptance criteria is ± 0.1 pH units of true value. All samples must be bracketed by an acceptable CCV. If the CCV is unacceptable, it may be re-analyzed one time.

10.3.4 If still unacceptable all samples analyzed since the last acceptable CCV must be re-analyzed.

10.3.5 A pH batch may be kept open to allow for analysis of samples later in the day. If a delay will occur, the current set of samples must be closed out with an appropriate CCV, then the set re-opened with another CCV at a later time.

10.4 Sample Preparation:

10.4.1 There is no preparation necessary for aqueous samples.

10.4.2 To 20 g of soil or waste sample (or 20 mL if the waste sample is fluid) in a 50-mL beaker, add 20 mL of reagent water cover and place on shaker table or continuously stir the suspension for at least 5 minutes. Different volumes can be prepared by maintaining approximately the 1:1 ratio. Additional dilutions are allowed if working with hygroscopic wastes or salts or other problematic matrices. Record weight/volume of material and volume of water in the pH logbook.

10.4.3 Allow the suspension to stand until most of the suspended material has settled out and decant the aqueous phase. Alternatively, filter or centrifuge off the aqueous phase for pH measurement. Record method of separation in the logbook.

10.4.4 If the supernatant is multiphasic, decant or filter the oily phase and measure the aqueous phase for pH.

10.5 Sample analysis:

10.5.1 Ensure the fill hole is uncovered when taking pH measurement and the electrolyte in the outer cavity is above the solution being measured to prevent reverse electrolyte flow.

10.5.2 Allow the sample to come to room temperature. If the temperature of the sample is not within ± 2°C of the buffer temperature, automatic temperature compensation (ATC) is required. The use of an ATC probe is required by OEPA.

10.5.3 Place the sample or buffer solution in a clean beaker using enough to cover the sensing elements of the electrode. A magnetic stirrer is used to help stabilize readings. Stir at a constant rate to provide homogeneity and suspension of any solids. Stirring rate should minimize the air transfer rate at the air/water interface (do not create a vortex) to minimize the entrainment of carbon dioxide.

10.5.4 Thoroughly rinse and if necessary, blot dry the electrode cage and ATC prior to placing it in the sample to minimize cross contamination. Allow sample readings to stabilize and record pH and temperature in the pH Logbook.

10.5.5 For replicate analysis, repeat measurement on successive aliquot(s) of sample until values differ by 0.1 or less pH units. Report final measurement.

10.5.6 If the pH measurement drops to less than 0.1 on the meter, immediately remove and rinse the probe to prevent any damage to the probe. Record result as less than 0.1 SU and enter zero in the LIMS for the final result.

10.5.7 For measurements that exceed the calibrated range of 2 to 12, use a pH buffer of 1 and 13 to check the probe performance. The acceptance criteria at the extreme end of the pH range should be ± 0.25 SU.

10.6 Maintenance:

10.6.1 The sensing bulb and junction in the electrode must not be allowed to dry out. The electrode should be stored at all time in pH 7.0 buffer when not in use. Alternatively, a pH 4.0 buffer can be used for storage.

10.6.2 The internal solution level in the probe must be maintained above the internal element and above the solution being measured at all times. Fill when low with manufacturer's electrolyte solution. Close fill hole when the probe is not in use to minimize crystallization of the electrolytic fluid.

10.6.3 Monthly: drain, flush with warm water, and refill the probe. After refilling, let the probe hang vertically in dry air for 15-30 minutes to wet the internal junction. Then store in buffer solution for 2 hours before using.

10.6.4 Clean the probe with warm water and detergent. If necessary, use dilute acid or solvents, such as alcohol or acetone, to remove grime and oil residue. Wiping the sensing bulb will remove the hydration layer on the bulb. Allow probe to soak in either a buffer 7 or 4 for 10 to 15 minutes to re-hydrate. Consult manufacturer instructions for additional detail.

10.6.5 Probe replacement may be required if the probe takes longer than a minute to stabilize in buffer solutions.

10.6.6 See the instructions that come with the electrodes as well as the instruction manual that comes with the meter for additional maintenance information. All maintenance shall be recorded in the pH Meter Maintenance Logbook.

10.7 Example Analysis Queue

- Buffer 2.0 (if applicable)
- Buffer 4.0
- Buffer 7.0
- Buffer 10.0
- Buffer 12.0 (if applicable)
- ICV Buffer 4.0
- CCV (Buffer 2, 4, 7, 10 or 12) if ICV is not used as the opening CCV
- Samples 1-10
- CCV (Buffer 2, 4, 7, 10 or 12)
- Samples 1-10
- CCV (Buffer 2, 4, 7, 10 or 12)

Additional CCVs are used at the discretion of the analyst and when there is a time elapse between samples. pH Buffers of 1 or 13 may be used as checks when extreme sample pH is encountered.

11.0 Calculations / Data Reduction

11.1 The reading/result is obtained from the pH meter. There are no sample calculations.

11.2 For results less than 0.1 SU, enter zero in the LIMS. The reported result will be <0.1 SU.

11.3 The LIMS will not make QC evaluations against a set pH value of 0.1 units. As such, all determinations as to whether or not the replicates are acceptable are done manually.

12.0 Method Performance

The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.1 **Demonstration of Capabilities** - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system. For drinking water, EPA 150.1 & SM 4500 H^+B are OEPA certified tests. Only certified analysts may perform this test for Ohio drinking water compliance purposes.

12.2 **Method Detection Limit Study** – MDL studies are not performed for this test.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.2 The following waste stream is produced when this method is carried out:

14.2.1 Acidic and/or alkaline sample waste and exhausted acidic and/or alkaline buffer solutions generated by the analysis is neutralized (to between pH 5-9) and discharged to the sanitary sewer.

15.0 References / Cross – References

15.1 Test Methods for Evaluating Solid Waste, EPA, 4th Edition, Method 9040C.

15.2 Test Methods for Evaluating Solid Waste, EPA, 4th Edition, Method 9045D.

15.3 Standard Methods, 4500 H^+B, 20th Edition.

15.4 Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised March 1983, Method 150.1, pH

15.5 Accumet Excel XL50 User Manual, Fisher Scientific.

15.6 DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton.

15.7 DT-QA-005 Procedure for Balance Calibration Check.

15.8 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.

16.0 Method Modifications

SOP Section	Method	Modification	Justification
7	N/A	Although not a method specification, Ohio EPA does not allow use of sealed probes. This had previously been interpreted as not allowing the use of GEL probes.	Refillable GEL probes are acceptable to Ohio EPA.

17.0 Attachments

None

18.0 Revision History

18.1 Revision Date

- 03/28/2008 Biennial review; Update for 2007 OEPA audit
- 03/29/2010 Biennial Review

18.2 Changes from last revision

Section	Change from	Change to	Reason
2.1	NA	Add EPA 150.1 is not currently approved for NPDES.	Moved from Section 19 which was deleted.

Section	Change from	Change to	Reason
3.1	pH is the measure of the acidity or alkalinity of a solution.	pH is the measure of the activity of the hydrogen ion in a solution. The greater the activity, the more acidic, the lesser the activity, the more basic the solution.	Clarity of method.
4.0	NA	Added additional interferences in 4.4 through 4.8.	Clarity of method.
6.0	NA	Added shaker table and centrifuge.	Accurately describe laboratory procedure.
7.3 9.2	Buffers 4.00, 7.00, & 10.00	Buffers 2.00, 4.00, 7.00, 10.0 & 12.00	Method compliance.
7.4	NA	ICV Buffer Solution.	Accurately describe laboratory procedure.
7.5	NA	Buffer Solutions of 1 & 13	Accurately describe laboratory procedure and to provide a pH check for samples outside the calibration range.
8.0	NA	Added table to Section 8 describing sample collection and preservation.	Compliant with new SOP format recommendations.
8.1	Aqueous samples should be collected with as little headspace as possible. Samples must not be preserved.	Aqueous samples should be collected with as little headspace as possible. Samples not at equilibrium with the atmosphere are subject to changes when exposed.	Clarity of method.
9.0	NA	Added table to Section 9 detailing QC controls.	Compliant with new SOP format recommendations.
10.1.1	The meter uses a three point calibration.	Calibration must include at a minimum the use of 2 standards that bracket the sample range.	Accurately describe laboratory procedure and clarify method.
10.1.2	NA	For methods 150.1 and SM4500 H-B, typically a 3 point calibration is performed using buffers 4, 7, 10.	Accurately describe laboratory procedure and clarify method.
10.1.3	NA	For methods 9040 & 9045, typically a 5 point calibration is performed using buffers 2,4,7,10,12.	Accurately describe laboratory procedure and clarify method.
10.3.1	The ICV may serve as the beginning CCV.	The ICV may serve as the beginning CCV if samples are analyzed shortly after calibration.	Accurately describe laboratory procedure and clarify method.
10.3.2	Standard buffer used for CCV . . . . should be used.	Added – One of the CCVs is used as the batch LCS. Indentify the LCS/CCV with the batch number.	Accurately describe laboratory procedure and clarify lab technique.

Section	Change from	Change to	Reason
10.5.6	NA	If pH measurement drops to <0.1 on the meter, immediately remove and rinse probe. Record result as <0.1 SU.	Accurately describe laboratory procedure.
10.5.7	NA	For measurements that exceed the calibration range of 2-12, use a pH buffer of 1 & 13.	Accurately describe laboratory procedure.
10.7	Example Run Sequence table	Example Run Sequence bullets	Accurately describe laboratory procedure and include QC requirements.
11.2	NA	For results less than 0.1, enter zero in the LIMS. The reported result will be <0.1.	Accurately describe laboratory procedure.
13.0 / 14.0	Section 13 – Waste Management and Pollution Control	Section 13 separated into two sections: Section 13 – Pollution Control and Section 14 – Waste Management	Compliant with new SOP format recommendations.
15.0	NA	Added additional QA SOPs to the References	Compliant with new SOP format recommendations.
16.0	NA	Method Modification – pH value reported does not specify the temperature at which the color was determined.	Accurately describe laboratory LIMS reporting.

Title: Paint Filter Liquids Test

SW - 846 Method 9095B

Approvals (Signature/Date):

Ron Paulick — 12/27/11 Department Manager — Date	Jason Lykins — 12/27/11 EH&S Officer — Date
Violet Fanning — 12/27/11 Quality Assurance Manager — Date	Tara Schlenker — 01/03/12 Laboratory Director — Date

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1.0 Scope and Application

1.1 This method is used to determine the presence of free liquids in a representative sample of waste, and may be used to determine compliance with 40 CFR 264.314 and 265.314.

1.2 This is a pass/fail test. Reporting Limits are not applicable.

1.3 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis as indicated in the QA Manual.

2.0 Summary of Method

A predetermined amount of material is placed in a paint filter. If any liquid passes through and drops from the filter within the five-minute test period, the material is deemed to contain free liquids.

3.0 Definitions

3.1 Please see the glossary in the QA Manual, DT-QAM-001, for additional definitions.

4.0 Interferences

4.1 Filter media may separate from the filter cone on exposure to alkaline materials.

4.2 Temperature can affect the tests results if the test is performed below the freezing point of any liquid in the same sample. Tests must be performed above the freezing point and can, but are not required to, exceed room temperature of 25°C.

4.3 As stated in the scope and application section of 9095B, the method is intended to determine the presence of "free liquids" in a sample. So if in fact the material does not actually contain any liquids, the result should be reported as compliant even though some fine particles pass through the filter. In these cases the sample should be flagged indicating the exact composition of the material that passes through the filter so that the data user is free to draw their own conclusion.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) 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

There are no materials used in this method which have a serious or significant hazard rating.

6.0 Equipment and Supplies

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

- *Conical Paint Filter:* Mesh number 60 ± 5% (fine meshed size).
- *Glass Funnel:* If the paint filter, with the waste, cannot sustain its weight on the ring stand, then a fluted glass funnel or glass funnel with a mouth large enough to allow at least 1 inch of the filter mesh to protrude should be used to support the filter. The funnel should be fluted or have a large open mouth in order to support the paint filter yet not interfere with the movement of the liquid that passes through the filter mesh into the graduated cylinder.
- *Ring Stand and Ring or a Tripod*
- *Container, such as a disposable beaker, weigh boat, graduated cylinder…*
- *Timer*

7.0 Reagents and Standards

Not Applicable

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waste	Plastic or Glass	100 ml/ gram	Cool ≤6.0 ^{o}C, but not frozen	None Defined	NA

8.2 A minimum of 100 mL or 100 gram representative sample is required for the test. If it is not possible to obtain a sample of 100 mL or 100 grams that is sufficiently representative of the waste, the analyst may use a larger size sample in multiples of 100 mL or grams, i.e. 200, 300, etc. However, when larger samples are used, analysts shall divide the sample into 100 mL or gram portions and test each portion separately. If any portion contains free liquids, the entire sample is considered to have free liquids. If the sample is measured volumetrically, then it should lack major air spaces or voids.

9.0 Quality Control

9.1 Perform one Sample Duplicate per batch.

9.1.1 A Duplicate is brought through the whole sample preparation and analytical process.

9.1.2 The Duplicate is acceptable if results match that of the sample.

10.0 Procedure

10.1 Assemble test apparatus as shown in Figure 1.

10.2 Obtain a representative 100 mL or 100 gram sample. If it is not possible to obtain a sample of 100 mL or 100 grams that is sufficiently representative of the waste, the analyst may use a larger size sample in multiples of 100 mL or grams, i.e. 200, 300, etc. However, when larger samples are used, analysts shall divide the sample into 100 mL or gram portions and test each portion separately. If any portion contains free liquids, the entire sample is considered to have free liquids. If the sample is measured volumetrically, then it should lack major air spaces or voids.

10.3 Place sample in the filter - "start" time is now. Record start time in logbook. Use of timer is optional.

10.3.1 A funnel may be used to provide support for the paint filter.

10.3.2 If the sample is of such light bulk density that it overflows the filter, then the sides of the filter can be extended upward by taping filter paper to the inside of the filter and above the mesh.

10.4 In order to assure uniformity and standardization of the test, material such as sorbent pads or pillows which do not conform the shape of the paint filter, should be cut into small pieces and poured into the filter.

10.4.1 Sorbents enclosed in fabric should be mixed with the resultant fabric pieces.

10.4.2 Particles to be tested should be reduced smaller than 1 cm.

10.4.3 Grinding is not acceptable, as it may produce fine particles that would not normally exist.

10.5 For brittle materials larger than 1 cm that do not conform to the filter, light crushing to reduce oversize particles is acceptable if it is not practical to cut the material.

10.6 Allow sample to drain for 5 minutes to 5 minutes 30 seconds from "start", into the receiving container.

10.7 If any portion of the test material collects in the container in the five minute period, then the material is deemed to contain free liquids for purposes of 40 CFR 264.314 and 265.314. The test is reported as "non-compliant".

NOTE: If only fine particles (no liquid) passes through the filter, then the result should be reported as compliant. Please see section 4.3 for discussion.

10.7.1 A "non-compliant" test is one in which the sample drips through the filter.

10.7.2 A "compliant" test is one in which the sample does not drip through the filter in the allotted time period.

10.7.3 Once a sample drips through, additional time is not required. Report the sample as "non-compliant".

10.7.4 If a sample has processed for longer than 5 minutes, but is still found to be "compliant", it may be reported as "compliant" without qualification.

10.7.5 If a sample drips, but has been sitting for more than the allotted time period, it must be reprocessed.

- If it can not be reprocessed, the data must be flagged.

11.0 Calculations / Data Reduction

Not Applicable

12.0 Method Performance

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study (MDL) - MDLs are not applicable to this test.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health & Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

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 accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.1 The following waste stream is produced when this method is carried out:

- Acidic or Alkaline waste is neutralized and discharged into the sanitary sewer.
- Disposable materials are disposed of in the general trash.

15.0 References / Cross - References

15.1 Method 9095B, Test Methods for Evaluating Solid Waste, SW-846 Revised November 2004.

15.2 DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton

15.3 DT-QA-005 Procedure for Balance Calibration Check

16.0 Method Modifications:

SOP Section	Method Reference	SOP Modification
Section 6	Graduated Cylinder	Use a container, like a disposable beaker or weigh boat- this allows for easier set up and requires less glassware cleaning.

17.0 Attachments

Figure 1: Paint Filter Test Apparatus Set-up.

18.0 Revision History

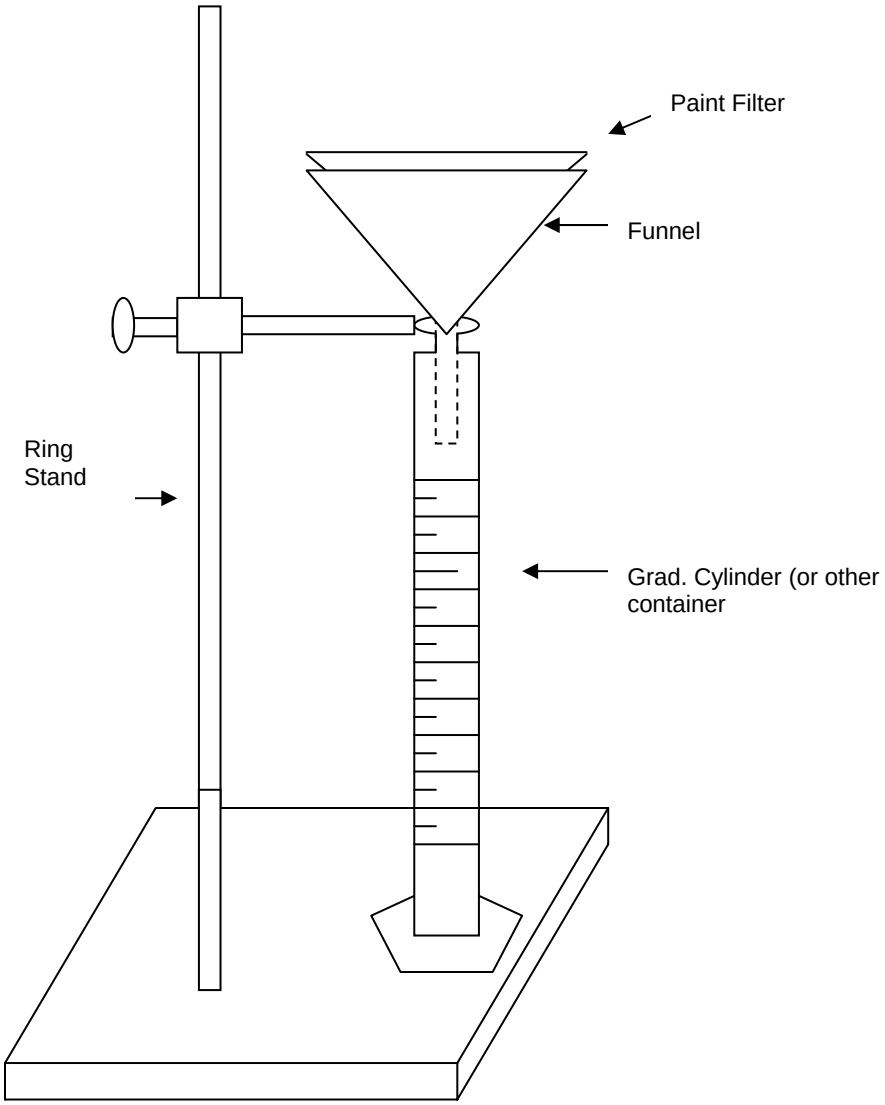
18.1 Revision dates

- 01/03/2012 - Biennial review
- 12/15/2009 - Biennial review
- 10/22/2007 - Original

18.3 Changes from last revision

Section	Change from	Change to	Reason
Title	9095A/B	9095B	9095B is current method
Copyright	2009 info	2012 info	Coypright is updated annually
2.0	If any portion of the material passes through . . .	If any liquid passes through . . .	Accurately describe the test.
3	Batch definition	Removed	Only test specific definitions are needed
3	Added	Please see the glossary in the QA Manual, DT-QAM-001, for additional definitions.	Consistency with current SOP format
4.3	The result will be reported as *negative* even though some fine particles pass through the filter.	The result will be reported as *compliant* even though some fine particles pass through the filter.	Accurately describe reporting practice
6.0	NA	Timer	Flexibility for analyst
8	Paragraph format	Table format	Consistency with current SOP format
8.3	NA	Temperature requirements.	Accurately describe laboratory practice
10.3	Place sample in filter – start time is now.	Place sample in filter – start time is now. Record start time in logbook. Use of timer optional.	Accurately describe laboratory practice
15.2	Method 9095A	Deleted	Method 9095B is followed
15	Added	DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton DT-QA-005 Procedure for Balance Calibration Check	Reflect ancillary references

Figure 1 Paint Filter Test Apparatus Set-up



Title: Total Suspended Solids & Total Volatile Suspended Solids

Standard Method 2540 D & E

Approvals (Signature/Date):

6/2/11 Ron Paulick Date Department Manager	6/2/11 Jason Lykins Date EH& S Officer
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1.0 Scope and Application

1.1 This SOP is applicable to aqueous matrices; drinking, surface and saline waters, domestic and industrial wastes.

1.2 Current default reporting limits are in the Laboratory Information Management System (LIMS). Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory specific method detection limit (MDL) data, project specific Data Quality Objectives (DQOs) and regulatory requirements are all taken into account.

1.3 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis as indicated in the Quality Assurance Manual.

2.0 Summary of Method

A well-mixed aliquot of the sample is filtered through a standard glass fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. If volatile solids are to be determined, the residue is ignited in a 550°C muffle furnace for 20 minutes.

3.0 Definitions

3.1 The term “Dissolved Solids”, also defined as filterable residue, is the portion of solids that passes through a filter and is the residue that remains after being evaporated to dryness under specified conditions.

3.2 The term “Suspended Solids”, also defined as non-filterable residue, is the portion of solids that is retained on a filter.

3.3 The term “Total Solids”, also defined as total residue, applies to the material of sample that is left in a vessel after evaporation and drying in an oven. Total solids include the suspended solids that would be retained by a filter and the dissolved solids that would pass through a filter.

3.4 The term “Volatile Solids”, also defined as volatile residue, is the portion of solid residue after drying that is lost after ignition.

3.5 Please see the glossary in the Quality Assurance Manual DT-QAM-001, for additional definitions.

4.0 Interferences

4.1 Floating oil and grease should be dispersed and included in the sample. Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

4.2 Exclude large floating particles or submerged agglomerates of non-homogeneous materials from the sample if it is determined that their inclusion is not representative.

4.3 Prolong filtration times resulting from filter clogging may produce high results owing to increased colloidal materials captured on the clogged filter.

4.4 Smaller volumes of sample may be required if there is sufficient suspended material clogging the filter or filtration takes longer than 10 minutes.

4.5 Samples high in dissolved solids may require additional washings to thoroughly wash the filter to ensure the removal of dissolved materials.

4.6 Limit sample size to that yielding no more than 200 mg residue as excessive residue on the filter may from a water-entrapping crust.

4.7 Temperature can affect weight lose due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat induced chemical decomposition.

4.8 After drying, residues are often very hygroscopic and will rapidly adsorb moisture from the air. Minimize opening desiccator to avoid moist air entering. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

4.9 Samples must be well mixed to achieve accurate results.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) 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

Be very careful when putting in and getting out samples from the muffle furnace. It is very hot, wear heat resistant gloves and use tongs.

5.2 Primary Matrerials Used

There are no materials with a health rating of 3 or 4 used in this method. **Note: This list does not include all materials used in the method. .** 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.

6.0 Equipment and Supplies

6.1 The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.2 Class A graduated cylinders.

6.3 Pipettes, wide bore.

6.4 Stir plate and magnetic stirrers.

6.5 Suction flask and filtration apparatus with reservoir and coarse fritted disk.

6.6 Filters, 934-AH or ProWeigh Filters.

6.7 Aluminum pans.

6.8 Analytical balance capable of weighing to 0.1 mg.

6.9 Desiccator, with color change desiccant.

6.10 Drying oven for operation at 103 to 105°C.

6.11 Muffle furnace for operation at 550°C.

7.0 Reagents and Standards

7.1 Lab weights to check balance. The lab weights are checked against ASTM Class 1 weights by the QA department on a monthly basis.

7.2 DI water, residue free.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time*	Reference
Aqueous	Plastic or Glass	200 ml	Cool $\leq$ 6.0^{o}C, but not frozen	7 days	SM 2540 – 20th ED

* Hold time is met when the sample has been filtered and placed in the oven.

9.0 Quality Control

9.1 The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 per preparation batch[1]	< MRL
Duplicate (DUP)[2]	1 per 10 samples	$\leq$ 10%

[1]A preparation batch is limited to 20 samples

[2]The DUP is randomly selected, unless specifically requested by a client.

9.2 Method Blank (MB): The MB is a de-ionized water blank that is prepared and analyzed with each preparation batch.

9.2.1 The MB must meet the acceptance criteria otherwise the batch must be re-prepared and re-analyzed.

9.2.2 If the MB has a hit, but the associated samples are less than RL, then reanalysis is not required.

9.3 Duplicate (DUP): The DUP is an additional aliquot of a sample that is carried through the process and analyzed. A DUP is prepared for every 10 samples.

10.0 Procedure

10.1 Balance Verification

10.1.1 Verify balance on a daily basis with bracketing lab weights.

10.2 Prepare filters.

10.2.1 Prepare filters by inserting filter disk with wrinkled side up in filtration apparatus. Apply vacuum and washing disk with three successive 20-mL volumes of DI water. Continue suction to remove all traces of water. Discard washings.

10.2.2 Remove filter from filtration apparatus and transfer to an inert aluminum pan. Dry in an oven at 103 -105°C for the minimum of 1 hour.

10.2.3 Cool in desiccator to balance temperature and weigh.

10.2.4 Repeat cycle of drying, desiccating and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less.

10.2.5 Store in a desiccator until needed.

10.2.6 This procedure may be skipped if pre-prepared filters are used.

10.3 Select sample volume that will yield no more than 200 mg residue.

10.4 Total Suspended Solids Sample Analysis (large volume).

10.4.1 For samples requiring a volume of 25 mL or greater, measure with the appropriate graduate cylinder.

10.4.2 Weigh filter and record the weight in the bench sheet and the pan identification. Alternatively, weigh filter and pan if the sample causes the filter to stick to the pan.

10.4.3 Assemble filtering apparatus and insert filter disk with wrinkled side. Begin suction and wet filter with a small volume of DI water to seat it.

10.4.4 Mix sample well and measure a 200 mL aliquot of sample using a graduated cylinder. Pour aliquot onto a glass-fiber filter with applied vacuum. The filtrate may be used for determination of total dissolved solids.

10.4.5 Wash graduate cylinder with three successive 10-mL volumes of DI water, allowing complete drainage between washings. Rinse sides of filter apparatus three times with DI water allowing complete drainage between rinsing. Continue suction for about 3 minutes after filtration is complete.

10.5 Total Suspended Solids Sample Analysis (small volume).

10.5.1 For samples that appear high in suspended solids that will require a volume less than 25 mL, use a wide bore pipet.

10.5.2 Assemble filtering apparatus and insert filter disk with wrinkled side. Begin suction and wet filter with a small volume of DI water to seat it.

10.5.3 Stir sample with a magnetic stirrer and pipet a well-mixed sample onto a glass-fiber filter with a wide bore pipet. For homogeneous samples, pipet from the approximate midpoint of the container but not in the vortex. Choose a point both mid-depth and midway between wall and vortex. Centrifugal force may separate particles by size and density resulting in poor precision when point of sample withdrawal is varied.

10.5.4 Wash with three successive 10-mL volumes of DI water, allowing complete drainage between washings. Rinse sides of filter apparatus three times with DI water allowing complete drainage between washings. Continue suction for about 3 minutes after filtration is complete.

10.6 Carefully remove filter and transfer to an aluminum pan as a support.

10.7 Dry filters in an 103 to 105°C drying oven overnight (minimum of 12 hours).

10.8 Transfer to desiccator to cool to room temperature.

10.9 Weigh the filter and record the weight in the bench sheet.

10.10 Alternatively, the filter and aluminum pan can be removed one hour after being placed in the drying oven, cooled in a dessicator, weighed and returned to the oven for 1 hour.

Remove from oven, cool in the desiccator, and weigh filter. This result may be used if the weight change between the successive weighing is ± 0.5 mg, or 4%, whichever is less.

10.11 Repeat step 10.10 if the weight change criterion is not met initially. Flag the data with an "S13" qualifier if the weight change criterion is not met after the third drying.

10.12 Determination of volatile solids.

10.12.1 Transfer the filter and aluminum pan to a 550 ± 20°C muffle furnace and ignite for 20 minutes.

10.12.2 Remove from muffle furnace and allow most of the heat to dissipate before placing the aluminum pan into the desiccator. Cool to room temperature in desiccator.

10.12.3 Weigh the filter and record the weight in the bench sheet.

10.12.4 Return the filter and aluminum pan to the muffle furnace for 20 minutes. Remove from the furnace, cool in the desiccator, and weigh filter. This result may be used if the weight change between the successive weighing is ± 0.5 mg, or 4%, whichever is less.

10.12.5 Repeat step 10.12.4 if the weight change criterion is not met initially. Flag the data with an "S13" qualifier if the weight change criterion is not met after the third ignition.

10.12.6 Ignite a blank glass fiber filter along with the samples to serve as the method blank.

11.0 Calculations / Data Reduction

11.1 Total Suspended Solids (mg/L):

$$\text{Total Suspended Solids} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

Where: A = weight of filter and dried residue, in grams

B = weight of filter, in grams

11.2 Total Volatile Suspended Solids (mg/L):

$$\text{Total Suspended Solids L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

Where: A = weight of residue and filter before ignition, in grams

B = weight of residue and filter after ignition, in grams

11.3 Relative Percent Difference (RPD)

$$RPD = \frac{|C_1 - C_2|}{(C_1 + C_2/2)} \times 100\%$$

Where: C_1 = Measured Result of Sample

C_2 = Measured Result of Duplicate

11.4 Weight change calculation:

$$\frac{|B-A|}{A} \times 100\% \leq 4\% \quad \text{or} \quad |B-A| \leq 0.5 \text{ mg}$$

Where: A = weight of dried residue + dish

B = successive weight of dried residue + dish

12.0 Method Performance

12.1 Method Detection Limit Study – MDLs are not performed for this gravimetric procedure.

12.2 Demonstration of Capabilities - Prior to the analysis of samples, a demonstration of capabilities (DOC), as described in the TestAmerica Dayton QA Manual (DT-QAM-001), must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Training Requirements – Training requirements and documentation are described in the TestAmerica Dayton QA Manual (DT-QAM-001).

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.2 The following waste streams are produced when this method is carried out.

- Non-hazardous aqueous sample waste generated by the analysis. This is disposed of into the sanitary sewer.
- Filter and pan are disposed to the general trash.

15.0 References / Cross-References

15.1 Methods for the Chemical Analysis of Water and Wastes, Residue, Non-Filterable, Method 160.2, USEPA, EMSL EPA-60/4-079-020, revised 1971

15.2 Standard Methods for the Examination of Water and Wastewater, Total Suspended Solids, Method 2540D & E, 20th Edition, APHA.

15.3 TestAmerica Dayton QA Manual, DT-QAM-001.

15.4 TestAmerica Company Wide Environmental Health and Safety Manual, CW-E-M-001.

15.5 DT-QA-005 Procedure for Balance Calibration Check

15.6 DT-QA-006 Thermometer Calibration

15.7 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus

16.0 Method Modifications

Item	Method	Modification
8.0	SM 2540 A	Cool to < 6.0°C, instead of 4°C.
10.3	SM 2540 D, 3c	Using a graduate cylinder per EPA 160.2 to measure samples in place of pipet.
10.9 10.10.5	SM 2540 D, 3c	Limit the cycle of drying, cooling and weighing to three. If weighing criterion is not met after three dryings, flag "S13".

17.0 Attachments

None.

18.0 Revision History

18.1 Revision Dates

- 6/03//2011 Biennial review
- 5/27/2009 Original (replaces DT05-35.5)

18.2 Changes from last revision

Section	Change from	Change to	Reason
Title	Remove	EPA 160.2	Method no longer approved
Copyright	2009 information	2011 information	Copyright updated annually
1.2, 1.3, 1.4 4.4, 4.7, 4.9	Deleted 1.2, 1.3, 1.4	Moved them to 4.4, 4.7, 4.9	Complete instructions for the analyst and uniformity within the SOP.
7.1	NA	Added Lab weights to check balance.	NELAC compliance.
8	Cool <6.0˚C	Cool <6.0˚C, but not frozen Hold time met when filtered and placed in the oven.	Compliance with SOP formatting requirements.
9	RPD ≤ 5%.	RPD ≤ 10%.	Compliance with method.
10.1	NA	Added balance verification.	NELAC compliance.
10.5.3	NA	Added centrifugal force may separated particles size.	Complete instructions for the analysts.
10.7	Dry for one hour repetitively.	Dry overnight and weigh.	NELAC compliance.
10.10	Repeat drying until meet the acceptance criteria.	Alternatively, dry for one hour increments and meet the acceptance criteria.	Consistent with method and laboratory practice.
11.1, 11.2	Weight in mg.	Weight in grams.	Consistent with method and

Section	Change from	Change to	Reason
			laboratory practice.
11.4	Weight change calculation.	Added ≤ 4% to the calculation.	Consistent with method and laboratory practice.
15	Added	• DT-QA-005 Procedure for Balance Calibration Check • DT-QA-006 Thermometer Calibration • DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus	Ancillary equipment references

Title: Total Phosphorus and Ortho-phosphorus, Block Digestor

US EPA Method 365.2, Standard Methods 4500P B, E 20th Ed.

Approvals (Signature/Date):

Ronald Paulick	2/232011	Jason M. Lykins	2/232011
Ron Paulick Department Manager	Date	Jason Lykins EH& S Officer	Date
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1.0 Scope and Application

1.1 This method covers the determination of specified forms of phosphorus in surface and saline waters, domestic and industrial wastes. This SOP is not applicable to drinking waters, as OEPA has indicated that the Block digestion is not acceptable to their agency.

1.2 The most commonly measured forms of phosphorus are reactive phosphorus or orthophosphate, acid-hydrolyzable phosphorus, and organic phosphorus. All three forms occur in either the dissolved or the suspended fractions. Insoluble forms of phosphorus are determined by calculation.

1.3 This procedure is based on HACH 8048 for reactive phosphorus, HACH 8180 for acid-hydrolyzable phosphorus and HACH 8190 for total phosphorus. These methods have been deemed equivalent to the referenced EPA and Standard Methods.

1.4 The methods are based on conversion of the various forms of phosphorus to the dissolved orthophosphate and colorimetrically determining the dissolved orthophosphate. Thus, depending on the prescribed pre-treatment and digestion of the sample, the various forms of phosphorus may be determined.

1.5 Calibration curves are based on the concentration of phosphorus in the standard. Results for orthophosphate or phosphate are calculated by multiplying the phosphorus concentration by 3.07.

1.6 The method is usable in the 0.02 to 1.10 mg of Phosphorus per liter range. Higher concentrations may be determined by sample dilution.

1.7 Current default reporting limits are in the Laboratory Information Management System (LIMS). Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory specific method detection limit (MDL) data, project specific Data Quality Objectives (DQOs) and regulatory requirements are all taken into account.

1.8 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis as indicated in the Quality Assurance Manual.

2.0 Summary of Method

2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of orthophosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the concentration of orthophosphate as phosphorus .

2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion.

2.3 Dissolved phosphorus samples are filtered through a 0.45-micron filter before analysis.

3.0 Definitions

3.1 Orthophosphorus (P, ortho): phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample are termed “reactive phosphorus”. Reactive phosphorus is largely a measure of orthophosphate as phosphorus or orthophosphorus.

3.2 Hydrolyzable Phosphorus (P, hydro): as measured by the sulfuric acid hydrolysis procedure and minus pre-determined orthophosphorus.

3.3 Organic Phosphorus (P, org): as measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphorus.

3.4 Phosphorus (P): all of the phosphorus present in the sample and measured by the persulfate digestion procedure.

3.5 Dissolved forms of Phosphorus (P-D): that form of phosphorus present in the filtrate of a sample filtered through a 0.45 micron pore size filter prior to the means of measuring as mentioned above.

3.6 Please see the glossary in TestAmerica Dayton's Quality Assurance Manual (Document number DT-QAM-001) for additional definitions.

4.0 Interferences

4.1 High iron concentrations can cause precipitation of and subsequent loss of phosphorus.

4.2 Arsenate reacts with molybdate reagent to produce a blue color similar to that formed with phosphate. Concentrations of arsenate equal to or greater than phosphorus can interfere with the phosphorus determination.

4.3 Hexavalent chromium and nitrite can lower phosphorus results by 3% at concentrations of 1 mg/L to as much as 15% at concentrations of 10 mg/L.

4.4 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

4.5 Turbidity and color may cause inconsistent results because the acid in the powder pillows may dissolve some of the suspended particles and cause desorption of orthophosphate from the particles.

4.6 Standards used to create a calibration curve must be prepared the same as samples. The salts added during prep and digestion can increase the intensity of the color during the spectrophotometric analysis.

4.7 Commercial detergents often contain phosphorus and should never be used. All glassware should be washed with 1:1 HCl and rinsed with DI water. Dedicated glassware should be used for the determination of phosphorus.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) 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
Potassium Persulfate	Oxidizer	0.1 mg/m^3 - TWA	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
Sodium Hydroxide	Corrosive	2 mg/m^3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
[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 The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.2 A spectrophotometer suitable for measurements at 880 nm with a light path of 1 cm.

6.3 COD Reactor, with thermometer and timer (for 150 $\pm$ 5°C).

6.4 Disposable culture tubes 16 X 100 mm with phenolic caps.

6.5 Multiple range air displacement pipettes and tips.

6.6 Volumetric flasks, 50-200 mL.

6.7 pH paper, wide range.

6.8 0.45 µm Membrane filters, pre-washed: Wash filters by either running several 100 mL aliquots of DI Water through them or by soaking 50 filters in 2 L of DI Water for 24 hours or soaking 50 filters in 2 L of DI Water for 1 hour and changing the water and soaking an additional 3 hours.

7.0 Reagents and Standards

7.1 The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

7.2 Deionized Water: Prepare by passing water through a mixed bed of cation and anion exchange resins or an equivalent source. Use the deionized water for the preparation of all reagents, standards and dilutions.

7.3 Potassium Persulfate ($K_2S_2O_8$) Powder Pillows, Cat. No. 20847-69. Shelf life manufacturer expiration date.

7.4 Sulfuric acid solution, 1 N: Add 28 mL of concentrated H_2SO_4 to 500 mL DI water in 1 L volumetric flask. When cool, dilute to volume. Prepare every 6 months.

7.5 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in 600 mL DI water. Cool and dilute to 1 liter. Prepare every 6 months.

7.6 PhosVer3 Phosphate Reagent Powder Pillows, Cat. No. 21060-46, contains ascorbic acid, potassium pyrosulfate, and sodium molybdate. Shelf life manufacturer expiration date.

7.7 Standard Stock Solution (100 mg/L): Dissolve in DI water 0.4394 g of potassium dihydrogen phosphate (potassium phosphate monobasic), KH_2PO_4. Dilute the solution to 1000 mL; 1.0 mL = 0.10 mg P. Prepare yearly. May also be purchased pre-made.

7.8 Working Standard (10mg/L): Dilute 20 mL of Standard Stock Solution to 200 mL of DI Water. Prepare monthly.

7.9 ICV Stock Solution: Dissolve in DI water 0.4394 g of potassium dihydrogen phosphate, KH_2PO_4. Dilute the solution to 1000 ml; 1.0 mL = 0.10 mg P. This must be from a different source than the potassium dihydrogen phosphate used to make the standard stock phosphorus solution. Prepare yearly. May also be purchased pre-made.

7.10 ICV Working Standard (10mg/L): Dilute 20 mL of ICV Stock Solution to 200 mL of DI Water. Prepare monthly.

7.11 Hydrochloric Acid—ACS. 1:1 Mix 1 part HCl and 1 parts reagent water. This is used for glassware cleaning.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Orthophosphorus					
Water	Plastic or Glass	250 mL	Cool <6.0°C but not frozen pH should be 6 - 8	48 Hours	40 CFR Part 136
Phosphorus					
Water	Plastic or Glass	250 mL	H_2SO_4 pH < 2; Cool <6.0°C but not frozen	28 days	40 CFR Part 136

If dissolved phosphorus or orthophosphate is to be determined, the sample should be filtered within 15 minutes of collection prior to preservation.

9.0 Quality Control

9.1 The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 per preparation batch[1]	< RL
Laboratory Control Sample (LCS)	1 per preparation batch[1]	90-110%
Matrix Spike (MS)[3]	1 per 10 samples	Statistical Limits[2]
Duplicate (DUP)[3]	1 per preparation batch[1]	20% RPD

[1]Preparation batch is limited to 20 samples
[2]Statistical control limits are updated annually and are maintained in LIMS.
[3]The sample selection for MS/DUP is random, unless specifically requested by a client.

9.2 Calibration Curve: Individual calibration curves must be prepared for each form of phosphorus according to the preparatory method that is used to determine that form of phosphorus. The concentrations and preparation instructions are included in Figure 1.

Construct a calibration curve quarterly by plotting corrected absorbency values against mg/L standard. The correlation coefficient (r) must be $\geq$ 0.995 using all six calibration standards and a blank. Repeat calibration if the correlation coefficient requirements cannot be met.

9.3 Initial Calibration Verification Standard (ICV): The ICV is a second source standard, prepared in the same way as the samples, and used to validate the calibration curve. It is analyzed immediately following the calibration curve. Acceptance criteria is 90-110% Recovery. If the ICV does not meet this criterion, the curve must be re-prepared and re-analyzed.

9.4 Continuing Calibration Verification Standards (CCV): The CCVs are mid-level standards that are prepared in accordance with the samples, analyzed every 10 samples and at the end of the batch. Acceptance criteria is 90-110% Recovery. If the standard does not

meet this criterion, the samples run after the last passing CCV/CCB must be reanalyzed. Several CCVs should be prepared due to time limitations after coloring.

9.5 Continuing Calibration Blanks (CCB): The CCBs are DI water blanks that are prepared in the same way as the samples. They are run with each CCV. The CCBs concentration must be less than the reporting limit. If the CCBs do not meet this criterion, the samples run after the last passing CCV/CCB must be reanalyzed. Several CCBs should be prepared due to time limitations after coloring.

9.6 Method Blank (MB): A method blank is DI water that is prepared in the same way as the samples. If the MB does not meet the acceptance criteria, all samples in the batch must be re-prepared and reanalyzed. Depending upon when colored and size of batch, the Method Blank can serve as a CCB.

9.7 Laboratory Control Sample (LCS): The LCS is prepared in the same manner as the samples. If the LCS does not meet the acceptance criteria, all samples in the batch must be re-prepared and reanalyzed. Depending upon when colored and size of batch, the LCS can serve as a CCV.

9.8 Matrix Spike (MS): The MS is brought through the whole sample preparation and analytical process. MS is an additional aliquot of a sample that is spiked with 0.250 mL of the 10 mg P/L Working Standard, resulting in aqueous spike concentration of 0.50 mg/L as phosphorus.

9.9 Duplicate (DUP): Analyze a DUP per every batch of 20 samples or less. The DUP is prepared by analyzing an additional aliquot of a sample.

10.0 Procedure

10.1 Total Phosphorus – Persulfate Digestion

10.1.1 Using pH paper, check and record pH for preservation of all samples. If sample pH is greater than 2, flag samples accordingly. Record observations in the logbook.

10.1.2 Turn on and verify that the digestor block temperature reaches 150 ± 5°C. Record this temperature in the logbook.

10.1.3 Pipette 5.0 ml of sample or diluted sample into a vial.

10.1.4 Add 2.0 mL of 1 N sulfuric acid and 1 potassium persulfate packet into each tube. Cap and invert repeatedly to mix.

10.1.5 Load the samples into the digestor. Heat for 30 minutes.

10.1.6 Remove the vials from the digestor and place in a test tube rack to cool to room temperature.

NOTE: At this point, the digestate can be refrigerated if the sample is not going to be neutralized and colored.

10.1.7 Add 2.0 mL of 1N sodium hydroxide to solution to neutralize the acid content. Cap and invert repeatedly to mix.

10.1.8 Read sample on the spectrophotometer to obtain background absorbance for highly colored or turbid samples.

10.1.9 Add 1 Phosphate Reagent packet to each tube. Cap and invert repeatedly to mix.

10.1.10 Let tubes stand at least 2 minutes, but not longer than 8 minutes before reading on the spectrophotometer. Use timer to mark time.

10.2 Acid-hydrolyzable Phosphorus – Sulfuric Acid Digestion

10.2.1 Using pH paper, check and record pH for preservation of all samples. If sample pH is greater than 2, flag samples accordingly. Record observations in the logbook.

10.2.2 Turn on and verify that the digestor block temperature reaches 150 ± 5°C. Record this temperature in the logbook.

10.2.3 Pipette 5.0 ml of sample or diluted sample into a vial.

10.2.4 Add 2.0 mL of 1 N sulfuric acid into each tube. Cap and invert repeatedly to mix.

10.2.5 Load the samples into the digestor. Heat for 30 minutes.

10.2.6 Remove the vials from the digestor and place in a test tube rack to cool to room temperature.

NOTE: At this point, the digestate can be refrigerated if the sample is not going to be neutralized and colored.

10.2.7 Add 2.0 mL of 1N sodium hydroxide to solution to neutralize the acid content. Cap and invert repeatedly to mix.

10.2.8 Read sample on the spectrophotometer to obtain background absorbance for highly colored or turbid samples.

10.2.9 Add 1 Phosphate Reagent packet to each tube. Cap and invert repeatedly to mix.

10.2.10 Let tubes stand at least 2 minutes, but not longer than 8 minutes before reading on the spectrophotometer. Use timer to mark time.

10.3 Orthophosphorous

10.3.1 Using pH paper, check and record sample pH for all samples to ensure all are at neutral pH. If pH is neutral (6-8), proceed to sample analysis at Step 10.3.2. If pH is not neutral, complete steps 10.3.1.1 – 10.3.1.5 prior to sample analysis.

10.3.1.1 Transfer 50 mL of sample to an Erlenmeyer flask using dedicated glassware.

10.3.1.2 Add 2 to 3 drops of phenolphthalein indicator solution.

10.3.1.3 If sample turns pink after adding the indicator solution, discharge the pink color with 1N H_2SO_4.

10.3.1.4 If sample is clear after adding the indicator solution, neutralize to a faint pink color with 1N NaOH. Discharge the faint pink color with 1N H_2SO_4.

10.3.1.5 Record pH of 7 in logbook, make note that the pH was adjusted to neutral. Samples are now ready for analysis.

10.3.2 Pipette 10.0 ml of sample or diluted sample into a vial.

10.3.3 Read sample on the spectrophotometer to obtain background absorbance for highly colored or turbid samples.

10.3.4 Add 1 Phosphate Reagent packet to each sample. Cap and invert several times to mix.

10.3.5 Let tubes stand at least 2 minutes, but not longer than 8 minutes before reading on the spectrophotometer. Use timer to mark time.

10.4 Spectrophotometry:

10.4.1 Set wavelength to 880 nm.

10.4.2 Put a tube with DI water into the spectrophotometer. Zero the instrument.

10.4.3 Read samples, using the sequence specified in Section 10.5. Record the absorbance in the logbook.

NOTE: There will be a small amount of undissolved reagent that remains in the bottom of the tube. Take care that the sample is settled before reading it to avoid elevated results due to turbidity.

10.5 Example Analysis Queue

- DI Blank (zero instrument)
- 0.00 mg/L Standard
- 0.05 mg/L as P Standard
- 0.10 mg/L as P Standard
- 0.20 mg/L as P Standard
- 0.60 mg/L as P Standard
- 0.80 mg/L as P Standard
- 1.00 mg/L as P Standard
- ICV 0.50 mg/L as P
- MB
- LCS 0.50 mg/L as P
- 10 Samples
- MS
- DUP
- CCV
- CCB
- 10 Samples
- MS
- CCV
- CCB

11.0 Calculations / Data Reduction

11.1 Linear Regression (used for all calibrations) $y = ax + b$

where: y = Instrument response
a = Slope of the line (coefficient of x)
x = Concentration of calibration standard
b = The intercept

11.2 If a turbidity blank was utilized subtract the absorbance reading of the turbidity blank from the sample absorbance.

11.3 The concentration of the target analyte is determined from the entered absorbance values using linear regression. Samples with concentrations that exceed the linear range must be diluted with reagent water and the colorization step repeated.

11.4 Aqueous Sample Results:

Phosphorus (as P) in mg/L = mg/L from curve x DF

Where: DF = Dilution Factor

11.5 Conversion of P to PO_4:

$$PO_4 = P \times 3.07$$

11.6 Conversion of P to P_2O_5:

$$P_2O_5 = P \times 2.29$$

11.7 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

Insoluble Phosphorus (P-In) = (P)-(P-Diss).

Insoluble orthophosphate (P-In, ortho) = (P, ortho)-(P-Diss, ortho).

Insoluble Phosphorus (P-In,) = (P) - (P-Diss,).

11.8 % Recovery, ICV, CCV, LCS:

$$\% \text{ Recovery} = \frac{\text{Measured Concentration}}{\text{Known Concentration}} \times 100\%$$

11.9 % Recovery, MS/MSD:

$$\% \text{ Recovery} = \frac{(S - U)}{T} \times 100\%$$

Where: S = Spiked result
U = Unspiked result
T = Spike True Concentration

11.10 Relative Percent Difference (RPD)

$$RPD = \frac{|C_1 - C_2|}{(C_1 + C_2/2)} \times 100\%$$

Where: C_1 = Measured Concentration of Sample
C_2 = Measured Concentration of Duplicate

12.0 Method Performance

12.1 Method Detection Limit Study - A method detection limit (MDL) study, as described in the TestAmerica Dayton QA Manual (DT-QAM-001), must be performed initially, verified annually and any time a significant change is made to the analytical system.

12.2 Demonstration of Capabilities - Prior to the analysis of samples, a demonstration of capabilities (DOC), as described in the TestAmerica Dayton QA Manual (DT-QAM-001), must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Training Requirements – Training requirements and documentation are described in the TestAmerica Dayton QA Manual (DT-QAM-001).

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 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 Dayton's facility addendum.

14.2 The following waste streams are produced when this method is carried out.

- Aqueous waste is collected and tested for pH. If pH is less than 4 or greater than 9, the waste is neutralized prior to disposing to the sanitary sewer.
- Contaminated disposable glass or plastic materials utilized in the analysis is disposed of in the general trash.

15.0 References / Cross-References

15.1 Hach Method 8048, Phosphorus, Reactive (Orthophosphate), 06/03, Rev 2.

15.2 Hach Method 8180, Phosphorus, Acid Hydrolyzable Digestion, 06/03, Rev 2.

15.3 Hach Method 8190, Phosphorus, Total, 06/03, Rev 2.

15.4 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983, Method 365.2

15.5 Standard Methods for the Examination of Water and Wastewater, 20th Edition, APHA, 1992. Method 4500P B, E.

15.6 DT-QA-005 Balance Calibration Checks.

15.7 DT-QA-007 Use and Calibration Verification of Volumetric Dispenser Apparatus.

15.8 TestAmerica Dayton QA Manual, DT-QAM-001.

15.9 TestAmerica Company Wide Environmental Health and Safety Manual, CW-E-M-001.

16.0 Attachments

Figure 1 - Calibration Standard/ICV Preparation

17.0 Method Modifications

Section	Method	Modification
9.2	EPA 365.2	Curves prepared quarterly; validated with one LCS per batch per Standard Methods instead of two; within 10% of true value, not 2%.
1.3	Hach 8048 Hach 8180 Hach 8190	Laboratory uses a Hach equivalent method.

Section	Method	Modification
10.3.1.2	EPA 365.2	Phenolphthalein solution is used to adjust the pH instead of pH meter.
7.3, 10.1.4	EPA 365.2	Use potassium persulfate in place of ammonium persulfate.
9.1, 16.0	EPA 365.2	Use a 6-point curve per Standard Methods instead of a 9 point curve.

18.0 Revision History

18.1 Revision Dates

- 02/25/2011 Biennial review
- 02/25/2009 Original (replaces DT05-82.0)

18.2 Changes from last revision

Section	Change from	Change to	Reason
1.3	Procedure based on Hach 8190.	Procedure based on Hach 8048, Hach 8180, & Hach 8190.	Accurately identify the applicable methods.
1.5	NA	Calibration curves based on phosphorus concentration. The applicable phosphate is calculated by multiplying by 3.07	Accurately describe what is determined in the lab.
4.5	NA	Turbidity and color may cause inconsistent results.	Identify potential interferences.
4.6	NA	Standards should be prepared the same as samples.	Compliance with method requirements.
4.7	Don't use commercial detergents.	Don't use commercial detergents, use dedicated glassware washed with 1:1 HCl.	Identify potential interferences.
5.2	NA	HCl	Accurately describe hazards in the lab.
6.7	NA	Add pH paper wide range.	Accurately describe laboratory procedure.
7.11	NA	HCL 1:1	Accurately describe laboratory procedure.
8.0	Cool < 6˚C	Cool < 6˚C but not frozen.	Accurately describe laboratory procedure.
8.0	NA	Ortho-phos: pH 6-8	Accurately describe laboratory procedure.
10.1.1	Check sample pH, if >2 note sample records	Check sample pH, if >2 flag samples accordingly and	Accurately describe laboratory procedure.

Section	Change from	Change to	Reason
	and notify the PM.	record observations.	
10.2	NA	Add the Acid-hydrolyzable phosphorus digestion.	Accurately describe laboratory procedure.
10.3.1.1	Check sample pH. If 7, go to sample analysis. If pH is not 7, complete following steps.	Check sample pH with pH paper. If neutral (6-8), record pH and proceed to sample analysis. If pH is not neutral, complete steps 10.3.1.1-10.3.1.5.	Accurately describe laboratory procedure and clarity to procedure.
10.4	NA	Moved NOTE: from 10.3 to 10.4	Accurately describe laboratory procedure and clarity to procedure.
10.5	Example Analysis Queue	Example Analysis Queue – add MS and DUP to sequence.	Specified by NELAC audit.
11.1	Prepare calibration curve creating a plot using linear regression.	Linear Regression = $Y = ax + b$	Initial statement was redundant from Section 9.2. More accurately describe laboratory procedure.
15	NA	Added additional method references.	Accurately describe laboratory methods.
Figure 1	Calibration Standards: 0.5, 0.1, 0.25, 0.5, 0.75	Calibration Standards: 0.5, 0.1, 0.2, 0.6, 0.8, 1.0	To provide uniformity between the block curve the hot plate curve

Figure 1 Calibration Standard/ICV Preparation

Standard	Volume of Working Standard	Working Standard Concentration*	Final Volume	Final Concentration
Blank	DI Water	DI Water	50 mL	0.00 mg/L as P
Standard 1	0.25 mL	10 mg/L as P	50 mL	0.05 mg/L as P
Standard 2	0.50 mL	10 mg/L as P	50 mL	0.10 mg/L as P
Standard 3	1.0 mL	10 mg/L as P	50 mL	0.20 mg/L as P
Standard 4	3.0 mL	10 mg/L as P	50 mL	0.60 mg/L as P
Standard 5	4.0 mL	10 mg/L as P	50 mL	0.80 mg/L as P
Standard 6	5.0 mL	10 mg/L as P	50 mL	1.00 mg/L as P
ICV	2.5 mL	10 mg/L as P	50 mL	0.50 mg/L as P
LCS	2.5 mL	10 mg/L as P	50 mL	0.50 mg/L as P

* ICV Working Standard is used for the ICV.

Title: Cyanide (Easy Chem)

EPA 335.4, EPA 335.1, SW-9012B & SM4500-CN C, E, G, I

Approvals (Signature/Date):

6/30/10 Ron Paulick — Date Department Manager	6/30/10 Jason Lykins — Date EH&S Officer
6/29/10 Violet Fanning — Date Quality Assurance Manager	6/29/10 Deborah Lowe — Date Laboratory Director

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1.0 Scope and Application

1.1 This method covers the determination of cyanide by midi distillation with semi-automated colorimetric analysis of the distillate.

1.2 This procedure is applicable to aqueous and non-aqueous matrices.

1.3 Cyanide determined by this method is defined as Total Cyanide.

1.4 The standard reporting limit is 0.005 mg/L for aqueous samples (based on a 50 mL sample). The standard reporting limit is 0.125 mg/Kg for non-aqueous samples (based on a 2 gram sample). Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory-specific, method detection limit (MDL) data, project specific DQOs, regulatory requirement are all taken into account, as well as instrument-to instrument repeatability.

1.5 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in the Quality Assurance Manual.

2.0 Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a midi distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

2.2 The sample is analyzed using a Systea EasyChem Discrete Autoanalyzer. In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CnCl, by reaction with chloramine–T at pH less than 8 without hydrolysis to the cyanate. After the reaction is complete, a red-color complex is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm. To obtain colors of comparable intensity, it is essential to have the same salt content in both the samples and the standards.

3.0 Definitions

See the Glossary in the Quality Assurance Manual, DT-QAM-001, for additional definitions.

4.0 Interferences

4.1 Interferences are eliminated or reduced by using the distillation procedure.

4.2 Sulfides will distill over with cyanide and adversely affect the colorimetric procedures. Samples should be treated at the time of collection as sulfides will convert CN^- or SCN^-, especially at high pH. If a drop of sample on lead acetate test paper previously moistened with acetate buffer indicates the presence of sulfides, then the sample must be treated. There are various methods for treating samples; EPA 335.4 recommends powdered cadmium carbonate, SW9012B recommends bismuth nitrate and SM4500-CN B recommends powdered lead carbonate. For the following matrix, treat the sample accordingly:

- For drinking water samples, treat the samples with powdered cadmium carbonate. A yellow cadmium sulfide precipitate will form for samples containing sulfide.
- For non-potable water samples, treat the samples with powdered lead carbonate. A black lead sulfide precipitate will form for samples containing sulfide.

Repeat one of the above operations until a drop of the treated sample solution does not darken the lead acetate test paper. Avoid a large excess of either cadmium or lead carbonate and long contact time in order to minimize loss of complexation or occlusion of

cyanide on the precipitated material. Filter the solution through a dry 0.45 µm filter paper (if desired, the solution can be pre-filtered using a glass fiber filter) into a vacuum flask, and from the filtrate, measure the sample to be used for analysis. When particulate metal cyanide complexes are suspected, filter solution before removing sulfide. Reconstitute sample by returning filtered particulates to the sample bottle after sulfide removal. Lead acetate paper will detect sulfide concentration as low as 5 ppm. If necessary, lower concentrations of sulfide can be determined colorimetrically.

Some non-potable water samples may contain sulfur compounds that may decompose during distillation and may interfere with the analytical procedure by converting cyanide to thiocyanate. To avoid this potential interference, add lead carbonate to the absorption solution before distillation. Filter sample after distillation before proceeding with the colorimetric determination. Alternatively, use a scrubber between the distillation flask and the absorption flask.

4.3 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 antifoaming agent will prevent the foam from collecting in the condenser.

4.4 Oxidizing agents such as chlorine decompose most cyanides. Treat samples that test positive for chlorine with sodium arsenite.

4.5 High results may be obtained for samples that contain nitrate, nitrite or both. During distillation, nitrate and nitrite will form nitrous acid which will react with some organic compounds and form oximes. These compounds will decompose under test conditions and form HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and 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 Safety Concerns or Requirements

Ensure cooling water is turned on to the distillation unit, and that the vacuum is properly adjusted. Otherwise the samples may boil over and come into contact with the heating plates.

Potassium Cyanide will give off Hydrogen Cyanide (HCN) gas if combined with strong acids. Inhalation of CN gas can cause irritation, dizziness, nausea, unconsciousness and potentially death.

This procedure could involve repetitive motions which could cause stress and an illness for the employee. Employee must avoid carrying out this task for extended periods of time or the work must be split up among the employees where possible.

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 standards 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
Sulfuric Acid	Corrosive Oxidizer Dehydrator	1 mg/m3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Chloramine T Hydrate	Poison		May be harmful by inhalation, ingestion, or skin absorption. This material is irritating to mucous membranes and upper respiratory tract. Avoid contact and inhalation.
Pyridine	Flammable Irritant	5 ppm-TWA	Inhalation causes severe irritation to the respiratory tract. Symptoms of overexposure include headache, dizziness, nausea, and shortness of breath. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. Absorption through the skin may occur, resulting in toxic effects similar to inhalation. May act as a photosensitizer. Vapors cause eye irritation. Splashes cause severe irritation, possible corneal burns and eye damage.
Potassium Cyanide (present in CN standards)	Poison Corrosive	5 mg/m3 TWA as CN	This material will form Hydrogen Cyanide (HCN) gas when combined with strong acids. Breathing HCN gas may result in death. Corrosive to the respiratory tract. May cause headache, weakness, dizziness, labored breathing nausea and vomiting, which can be followed by weak and irregular heart beat, unconsciousness, convulsions, coma and death. Solutions are corrosive to the skin and eyes, and may cause deep ulcers, which heal slowly. May be absorbed through the skin, with symptoms similar to those noted for inhalation. Symptoms may include redness, pain, blurred vision, and eye damage.

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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Midi Distillation System: Lab Crest “Midi-Dist” Distillation System, Model 110-10

6.2 Systea EasyChem Discrete Analyzer system with the following components: sampling device, reaction cuvettes, pump, colorimetric detector, and PC for data collection

6.3 Plastic digestion cups, volumetric, 50 mL with certificate of volume accuracy. Environmental Express SC475 or equivalent.

6.4 Miscellaneous

- Miscellaneous laboratory glassware
- Macropipettes and micropipettes
- Sand
- Filter paper – glass fiber and 45µm
- Lead acetate test paper
- Potassium iodide starch test paper
- Dow Corning 544 antifoaming agent

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly. For the purpose of waste minimization or efficiency, the prepared volume of reagents may be more or less than stated below as long as the appropriate ratios of reagents are maintained to perform the analysis.

All standards/reagents should be stored at <6.0^{o}C but not frozen unless otherwise specified.

7.1 Reagent water: Deionized water.

7.2 Reagents for sample preparation.

7.2.1 Sodium Arsenite Crystals, Neat. Purchased. Store at room temperature.

7.2.2 Powdered Lead Carbonate. Purchased. Store at room temperature.

7.2.3 Powdered Cadmium Carbonate. Purchased. Store at room temperature.

7.2.4 Acetate Buffer. Dissolve 60.75 g of sodium trihydrate in DI Water and 117 mL of glacial acetic acid. Dilute to 250 mL with DI Water. Store at room temperature.

7.3 Reagents for cyanide distillation.

7.3.1 Sodium Hydroxide, 10N: Dissolve 400 g of NaOH in DI Water and dilute to 1 L with DI. Shelf life: 3 months. Store at room temperature.

7.3.2 Sodium Hydroxide, 0.25 N: This is an absorbing solution and sample wash solution. Measure 200 mL of 10N NaOH and dilute to 8 L with DI Water. Shelf life: 3 months. Store at room temperature.

7.3.3 Magnesium Chloride Solution, 51 % (w/v): Dissolve 510 g of $MgCl_2 \cdot 6H_2O$ in DI Water and dilute to 1 L. Shelf life: one year. Store at room temperature.

7.3.4 Sulfamic Acid 0.4N: Purchased shelf life: as listed by the manufacturer or 1 year. Dissolve 40 g H2SO3H in 1 L of DI water. Store at room temperature.

7.3.5 Sulfuric Acid, 50 % (v/v): Carefully add a portion of concentrated H_2SO_4 to an equal amount of DI Water. Shelf life: one year. Store at room temperature.

7.4 Reagents for cyanide amenable to chlorination.

7.4.1 Calcium Hypochlorite Solution: Dissolve 5 g of Calcium Hypochlorite crystals into DI Water and dilute to 100 mL. Shelf life: 1 year. Store at room temperature.

7.4.2 Sodium Hydroxide Solution, 1.0N: Dilute 100 mL of 10N NaOH to 1 L. Shelf life: 3 month. Store at room temperature.

7.4.3 Sodium Arsenite Crystals. (See 7.2.1)

7.5 Reagents for free or dissociable cyanide.

7.5.1 Acetic Acid 1+9. Mix 1 volume of glacial acetic acid with 9 volumes of DI water. Store at room temperature.

7.5.2 Acetate Buffer. Dissolve 410 g sodium acetate trihydrate in 500 mL DI Water. Add glacial acetic acid to yield a solution pH of 4.5. Store at room temperature.

7.5.3 Zinc Acetate Solution. Dissolve 120 g of zinc acetate in DI water and dilute to 1 L. Store at room temperature.

7.5.4 Methyl Red Indicator. Purchased. Alternatively, prepare by dissolving 0.02 g Methyl Red crystals into 60 mL of Reagent Alcohol. Add 40mL of DI Water. Store at room temperature.

7.6 Reagents for standardization.

7.6.1 Rhodamine Indicator: Purchased, alternatively dissolve 20 mg of p-dimethylaminobenzal-rhodamine in 100 mL acetone. Shelf life: Manufacturer's expiration date or 1 year if prepared.

7.6.2 Silver Nitrate Solution, 0.0192 N: Purchased. Shelf life: 1 year.

7.6.3 CN Standard Stock (from Potassium Cyanide) - 1000 mg/L: Purchased. Shelf life: Manufacturer's recommendation.

7.6.4 CN ICV Stock – 1000 mg/L: Purchased, alternatively prepare by dissolving 0.4907 g NaCN in Reagent Water and dilute to 500 mL. Shelf life: Manufacturer's recommendation or 1 year if prepared.

NOTE: The CN ICV Stock and CN Standard Stock are titrated upon receipt and periodically thereafter as follows: using silver nitrate (0.192 N) and a few drops of rhodamine indicator, titrate 10 mL Standard Stock Solution with a 25 mL burette, going from yellow to a pink color. Repeat by titrating the ICV Working Stock. Record in the standardization logbook.

7.6.5 CN Complex Standard Stock: – 1000 mg/L: Complex Cyanide, purchased. Shelf life: Manufacturer's recommendation or 1 year.

7.6.6 CN Working Standard - 5 mg/L: Prepare by pipetting 5 mL of CN Standard Stock into a 1L volumetric flask and diluting to the mark with 0.25N NaOH. Shelf life: 1 week.

7.6.7 CN Complex Working Standard - 5 mg/L: Prepare by pipetting 5 mL of CN Complex Standard Stock into a 1L volumetric flask and diluting to the mark with 0.25N NaOH. Shelf life: 1 year.

7.6.8 CN ICV Working Standard - 5 mg/L: Prepare by pipetting 1 mL of CN ICV Stock into a 200 mL volumetric flask and diluting to the mark with 0.25N NaOH. Shelf life: 1 week.

7.7 Reagents for colorimetric determination.

7.7.5 Sodium Hydroxide, 0.25 N: For use at the instrument. (See Section 7.3.2).

7.7.6 Phosphate Buffer Solution, 1 M: Dissolve 13.8 g of $NaH_2PO_4 \cdot H_2O$ in Reagent Water and dilute to 100 mL. This is Reagent 1 (R1). Shelf life: 1 year.

7.7.7 Chloramine-T: Purchased. Shelf life: one year.

7.7.8 Chloramine-T Solution: Dissolve 1.0 g of chloramine-T in Reagent Water and dilute to 100 mL. This is Reagent 2 (R2). Shelf life: Prepare weekly.

7.7.9 Pyridine Barbituric Acid Color Reagent Solution: Prepare this solution in a hood. Transfer 1.5g of barbituric acid into a Erlenmeyer flask. Add about 10 mL of Reagent Water and swirl the flask to mix. Add 7.5 mL of pyridine and 1.5 mL of concentrated HCl and mix until all of the barbituric acid is dissolved. Dilute to 100 mL with Reagent Water and store in amber glass container. This is Reagent 3 (R3). Shelf life: 6 months.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

8.2

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	Plastic or glass	250 mL	pH > 12 (6 NaOH pellets per L) Cool <6.0°C	14 days	40 CFR Part 136
Soil	Glass	4 oz	Cool <6.0°C	14 days	40 CFR Part 136

8.3 Oxidizing agents such as chlorine decompose most cyanides. Test a drop of the sample with potassium-iodide starch paper: a blue color indicates the need for treatment. Add sodium arsenite, a few crystals at a time, until a drop of samples produces no color on the indicator paper. Then add an additional scoop (approximately 0.6 g) of sodium arsenite for each liter of sample volume.

9.0 Quality Control

9.1 The following quality control samples are prepared for Total Cyanide by EPA 335.4.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 per preparation batch [1]	< RL
Laboratory Control Sample (LCS)	1 per preparation batch [1]	90-110%
Matrix Spike (MS) [2]	1 per 10 samples	90-110%
Duplicate (DUP) [2]	1 per 10 samples (potables) 1 per batch[1] (nonpotables and non-aqueous)	< 25% RPD

[1] A preparation batch is limited to 20 samples

[2] The MS and DUP are randomly selected, unless specifically requested by a client.

9.2 The following quality control samples are prepared for Total Cyanide by SW9012B.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 per preparation batch [1]	< RL
Laboratory Control Sample (LCS)	1 per preparation batch [1]	Statistical Limits (SW9012B)
Matrix Spike (MS) [2]	1 per 10 samples	Statistical Limits (SW9012B)
Duplicate (DUP) [2]	1 per batch[1]	< 25% RPD

[1] A preparation batch is limited to 20 samples

[2] The MS and DUP are randomly selected, unless specifically requested by a client.

9.3 For Cyanide Amenable to chlorination by EPA 335.1, SM4500CN-G, or SW9012B, there are no quality controls as chlorine destroys the available cyanide. The chlorinated prepared samples are run as total cyanides in a total cyanide batch but are not used for batch controls.

9.4 The following quality control samples are prepared for Free or Weak Acid Dissociable Cyanide by SM4500CN-I.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 per preparation batch [1]	< RL
Laboratory Control Sample (LCS)	1 per preparation batch [1]	Statistical Limits
Matrix Spike (MS) [2]	1 per 10 samples	Statistical Limits
Duplicate (DUP) [2]	1 per batch[1]	< 25% RPD

[1] A preparation batch is limited to 20 samples

[2] The MS and DUP are randomly selected, unless specifically requested by a client.

9.5 Method Blank: The Method Blank consists of a clean matrix that is taken through the analytical process.

9.5.1 If the method blank shows a detection above the required reporting limit, it must be reanalyzed. If this fails to correct the problem, all associated samples with must be re-digested.

9.5.2 If the associated samples are non-detect, then reanalysis of the Method Blank is not required.

9.5.3 If the concentration found in the samples is >10X the concentration found in the Method Blank, reanalysis is not required, but data must be flagged.

9.6 Laboratory Control Samples: The LCS consists of a clean matrix that is spiked and taken through the analytical process.

9.6.1 If percent recovery is outside the acceptance limits, all samples associated with the LCS must be reanalyzed.

9.6.2 If the LCS recovery is high and the associated samples are <RL, reanalysis is not required. Data must be flagged.

9.7 MS: An MS is a second aliquot of a sample that is spiked and taken through the analytical process.

9.7.1 For non-potable samples, the MS is not used for batch control. If criteria is not met, data is flagged.

9.7.2 For drinking water, if the MS recovery is out of limits, repeat the batch. If criteria is still not met, flag the data.

9.8 Duplicate: A Duplicate is a second aliquot of sample that is taken through the analytical process.

9.8.1 For non-potable samples, the Duplicate is not used for batch control. If criteria is not met, repeat parent and duplicate. If criteria is still not met, flag the data.

9.8.2 For drinking water, if the Duplicate RPD is out, repeat the batch. If criteria is still not met, flag the data.

10.0 Procedure

10.1 Cyanide Distillation

The procedure described here utilizes a midi distillation apparatus and requires a sample aliquot of 50 mL (or aliquot diluted to 50 mL) for aqueous samples and 2 grams for solid matrices. All samples are distilled. Calibration curves and CCVs are not.

More or less sample amount may be used depending on amount of sample provided, anticipated or known levels of analyte or interference, reporting limit requirements, or to meet other laboratory, client or regulatory needs.

10.1.1 Use lead acetate paper to check aqueous samples for the presence of sulfide. A positive test is indicated by a black color on the paper. If positive, treat the sample as stated in section 4.2 of this SOP and retest for sulfide. Continue this procedure until sulfide is no longer detected. If positive for sulfides, the data should be flagged accordingly.

10.1.2 Test samples for chlorine. If positive, treat according to Section 8.3.

10.1.3 For aqueous samples: transfer 50 mL of sample (or an aliquot diluted to 50 mL with 0.25 N NaOH) into the distillation flask, this is the “initial volume”.

10.1.3.1 For the Blank and LCS use 50 mL of 0.25N NaOH.

10.1.3.2 To the LCS, add 1 mL of Complex Working Standard. This results in a spike concentration of 0.10 mg/L.

10.1.3.3 For the MS take an additional 50 mL aliquot (or aliquot diluted to 50 mL with 0.25N NaOH) of the sample chosen for QC. To the MS, add 1 mL of CN Working Standard. This results in a spike concentration of 0.10 mg/L.

10.1.3.4 For the DUP, take an additional 50 mL aliquot (or an aliquot diluted to 50 mL with 0.25N NaOH) of the sample chosen for QC.

10.1.4 For solid samples: weigh 2.0 g of sample (to the nearest 0.01 g) the distillation flask, this is the “initial weight”, and dilute to 50 mL with 0.25 N NaOH.

10.1.4.1 For the Blank and LCS use 2 g of sand and bring to 50 mL with 0.25N NaOH.

10.1.4.2 To the LCS, add 1 mL of Complex Working Standard. This results in a spike concentration of 2.5 mg/Kg.

10.1.4.3 For the MS, take an additional two 2 g aliquot of the sample chosen for QC and bring to 50 mL with 0.25N NaOH. To the MS, add 1 mL of CN This results in a spike concentration of 2.5 mg/Kg

10.1.4.4 For the DUP, take an additional 2 g aliquot of the sample chosen for QC.

10.1.5 Add 50 mLs of 0.25 N NaOH to the gas absorber flask.

10.1.6 Connect the boiling flask, condenser, and absorber on the block.

10.1.7 Turn on the vacuum and adjust the gang valves to give a flow of 2-3 bubbles per second from the impingers in each reaction vessel.

10.1.8 After five minutes of vacuum flow, inject 5 mL of sulfamic acid solution through the air inlet tube of the distillation head into the reaction vessel.

10.1.9 Inject 5 mLs of 50 % H_2SO_4 through the top air inlet tube of the distillation head into the reaction vessel. Allow mixing for five minutes. Note: the acid volume must be sufficient to bring the sample pH to below 2.

NOTE: Do not open the vessel to check the pH. Cyanide may escape at this stage of the process.

10.1.10 Add 2 mLs of magnesium chloride solution through the top air inlet tube of the distillation head into the reaction vessel. Excessive foaming from samples containing surfactants may be quelled by the addition of another 2 mL of magnesium chloride solution or the use of an antifoaming agent.

10.1.11 Turn on the distillation apparatus and set for 105 minutes. Heat the samples to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

10.1.12 After 105 minutes, the unit will turn off the heat. Continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.

10.1.13 After cooling, close off the vacuum at the gang valve and remove the absorber.

10.1.14 Pour the distillate into a calibrated digestion tube and bring up to 50 mL volume with 0.25N NaOH solution if necessary, this is the “final volume”. Cap the tube and store at <6.0^{o}C but not frozen, prior to analysis.

10.2 **<u>Pretreatment of Cyanides Amenable to Chlorination</u>**

10.2.1 The test must be performed under amber or incandescent lighting or under a box. Wrap glass container with aluminum foil and/or put containers under a box to shield the samples from fluorescent lighting. $K_3[F_3\text{-}(CN)^6]$ may decompose under UV light and hence will test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination.

10.2.2 To one 50 mL sample or to a sample diluted to 50 mL, add calcium hypochlorite solution drop-wise while agitating and maintaining the pH between 11 and 12 with 1.0N sodium hydroxide until an excess of chlorine is present as indicated by potassium iodide starch paper turning blue. The sample will be subjected to alkaline chlorination by this step.

CAUTION: The initial reaction product of alkaline chlorination is the toxic gas cyanogens chloride; therefore, <u>it is necessary that this reaction be performed in a hood.</u>

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

10.2.4 After one hour, add solid sodium arsenite until KI-starch solution shows no residual chlorine.

10.2.5 Analyze the total cyanide concentration of both chlorinated and the unchlorinated samples by the method described in Section 10.1. The difference between the total cyanide concentration in the chlorinated and unchlorinated samples is equal to the cyanide amenable to chlorination.

10.3 **Preparation for Weak Acid Dissociable**

10.3.1 Perform steps 10.1.1 through 10.1.7. Use the CN Working standard in place of the Complex Working Standard.

10.3.2 Add 2 mL of Sodium acetate solution through the air inlet.

10.3.3 Add 2 drops of Methyl red indicator.

10.3.4 Add 2 mL of Zinc acetate solution through the air inlet. If necessary, rinse air inlet tube with DI Water and let air mix contents.

10.3.5 If the solution is not pink, add Acetic Acid (1+9) drop-wise through the air inlet until a pink color persists.

10.3.6 Turn on the Midi distillation heaters and heat for 105 minutes.

10.3.7 After heating for 105 minutes, the unit will turn off the heat. Continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.

10.3.8 After cooling, close off the vacuum at the gang valve and remove the absorber.

10.3.9 Pour the distillate into a calibrated digestion tube and bring up to 50 mL volume with 0.25N NaOH solution if necessary, this is the “final volume”. Cap the tube and store at <6.0^{o}C but not frozen, prior to analysis.

10.4 **Cyanide Analysis (Instrument Calibration and Analysis)**

10.4.1 Set up

10.4.1.1 Select EasyChem icon to open data acquisition software. When the system has been properly initialized a message box will display “Analyzer Ready”.

10.4.1.2 Fill the wash water bottle with fresh DI Water; insert the wash tube into the bottle.

10.4.1.3 Close the peristaltic pump located on the right side of the analyzer, by pressing the pump plate upwards and screwing the plate knob.

10.4.1.4 Empty waste container, if necessary.

10.4.1.5 Initiate filters auto zero function insuring all values fall into specified ranges. To ensure good results, visually check that the wash water is being pumped out of the bottle and that there are no air bubbles.

10.4.1.6 Select the appropriate Cyanide method on the instrument.

10.4.1.7 Fill containers for Reagent 1, 2 and 3 and place in their specified position in the Cyanide method.

10.4.1.8 Place all required QC and samples into the sample tray. Input information required by the data acquisition software.

10.4.1.9 Proceed with analysis of samples and quality control samples using predefined methods. Please see Section 9 for QC frequency and acceptance limits.

10.4.2 Initial Calibration

10.4.2.1 A curve must be generated every six months, at a minimum. The calibration curve is constructed without forcing the curve through the origin. The blank can be used as a point on the curve for the value of zero.

10.4.2.2 Prepare Initial Calibration Standards as in Table 1.

10.4.2.3 Analyze the calibration curve standards in order of decreasing concentration.

10.4.2.4 The automated instrument software will construct a calibration curve (without forcing through zero) and calculate a correlation coefficient.

10.4.2.5 The calibration coefficient must be $\geq$ 0.995 using the calibration standards.

10.4.2.6 If this correlation coefficient cannot be achieved, the calibration and sample analysis must be repeated.

10.4.3 Initial Calibration Verification (ICV)

10.4.3.1 The ICV standard is a second source standard analyzed immediately after the calibration curve to verify the calibration.

10.4.3.2 See Table 1 for ICV preparation.

10.4.3.3 The ICV acceptance criteria is recovery of 90 - 110%. If this criterion cannot be met, repeat the calibration.

10.4.4 Initial Calibration Blank (ICB)

10.4.4.1 An Initial Calibration Blank (ICB) is a 0.25N NaOH Blank that must be run with each ICV.

10.4.4.2 The ICB must be less than the reporting limit.

10.4.4.3 Repeat the calibration and analysis if the ICB is not less than the reporting limit.

10.4.5 Proceed with analysis of samples and quality control samples using manufacturer's autosampler protocols.

10.4.6 Continuing Calibration Verification (CCV)

10.4.6.1 A Continuing Calibration Verification (CCV) must be analyzed after every ten samples and at the end of the analytical run.

10.4.6.2 See Table 1 for CCV preparation.

10.4.6.3 The CCV standard acceptance criteria is recovery of 90 - 110%. If this criterion cannot be met, all samples analyzed since the last passing CCV must be reanalyzed.

10.4.6.4 If the CCV recovery is high and the associated samples are <RL, the data may be reported, but must be flagged.

10.4.7 Continuing Calibration Verification Blank (CCB)

10.4.7.1 A Continuing Calibration Blank (CCB) is a 0.25N NaOH blank that must be run with each CCV. The CCB must be less than the reporting limit.

10.4.7.2 If the CCV or CCB requirements cannot be met, repeat all samples since the last acceptable CCB/CCV pair.

10.5 **Example Analysis Queue**

- CCB
- Std 0.300
- Std 0.100
- Std 0.030
- Std 0.010
- Std 0.005
- CCB
- ICV
- CCB
- CCV
- CCB
- MB
- LCS
- Samples (up to 10)
- MS
- DUP
- CCV
- CCB
- Samples (up to 10)
- MS
- DUP (potable only)
- CCV
- CCB

11.0 Calculations / Data Reduction

11.1 Prepare a calibration curve for each analyte by plotting instrument area response against standard concentration using the instrument software.

11.2 Response Factors (RF) = $\frac{\text{Absorbance}}{\text{Concentration of Standard}}$

11.3 Linear Regression (used for all calibrations): $y = ax + b$

where:

y = Instrument response

a = Slope of the line (coefficient of x)

x = Concentration of calibration standard

b = The intercept

11.4 Relative Percent Difference (RPD) between Duplicates:

$$RPD = \frac{(\text{Larger Value} - \text{Smaller Value}) \times 100}{(\text{Average of the Values})}$$

11.5 Spike Recovery of LCS / MS:

$$\%\,\text{Recovery} = \frac{(S - U) \times 100)}{T}$$

Where:
S = Spiked result
U = Unspiked result (use 0 for LCS)
T = Spike True Concentration

11.6 Sample results - raw

$$\text{Conc "raw" (mg/L)} = \frac{(A - \text{Intercept})}{(\text{Slope})}$$

where:
A = Absorbance
Slope = Slope of curve

11.7 Sample results- Aqueous

$$\text{Conc Aqueous (mg/L)} = \frac{(C)\ (Vt)\ (D)}{(Vs)}$$

where:
C = Raw concentration calculated by instrument (see 11.5)
D = Dilution factor
Vt = Final volume, in L (as per 8.1.14)
Vs = Initial volume, in L (as per 8.1.3)

11.8 Sample results- Non-Aqueous

$$\text{Conc Non-Aqueous (mg/kg)} = \frac{(C)\ (Vt)\ (D)}{(Ws)} * 1000$$

where:
C = Raw concentration calculated by instrument
D = Dilution factor
Vt = Final volume, in L (as per 8.1.14)
Ws = Initial weight, in g (as per 8.1.4)

12.0 Method Performance

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples.

12.2 Demonstration of Capabilities - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical procedure.

12.3 Method Detection Limit - A MDL study as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.4 Linear Calibration Range – Conduct an LCR study for each instrument/analyte combination and keep on file.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health & Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.2 The following waste stream is produced when this method is carried out:

- Wastewater containing 1.5% Pyridine is drummed and disposed of through a Waste Handler.
- Contaminated disposable materials utilized for the analysis are disposed of in the general trash.

15.0 References / Cross-References

15.1 Systea EasyChem, Software Operation Manual.

15.2 Instruction Manual, Lab-Crest" Midi-Dist" Distillation System, Model 110-10.

15.3 EPA 335.4 USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, Document # ILM04.0, EPA-540/R-95/121, 1995.

15.4 EPA 335.1, 1974.

15.5 SW846 9012B, Revision 2, November 2004.

15.6 Standards Methods 4500-CN C, E, G & I, 20th Edition.

15.7 DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton

15.8 DT-QA-005 Procedure for Balance Calibration Check

15.9 DT-QA-006 Thermometer Calibration

15.10 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus

16.0 Method Modifications

Item	Method	Modification
11.5 7.2.5	EPA 335.4, SW9012B	The samples are heated for 105 minutes per manufacturer's instructions.
4.2 3.3	EPA 335.4, SW9012B	Use lead carbonate instead of cadmium carbonate or bismuth nitrate for nonpotable aqueous samples.
4.4	EPA 335.4	Use sodium arsenite to treat chlorinated samples instead of ascorbic acid.
4.1 7.1.2	EPA 335.1, SW9012B	Use 50 mL instead of 500 mL

17.0 Attachments

Table 1. Calibration Standard/ICV Preparation

Table 2. Method Comparisons

18.0 Revision History

18.1 Revision Dates

- 6/30/2010 - Biennial Review
- 6/27/2008 - Original

18.2 Changes from last revision

Section	Change from	Change to	Reason
Copyright	2008 information	2010 information	Corporate change to template
Section 4	Sulfide treated with lead carbonate.	Sulfide treated with cadmium carbonate for drinking water and lead carbonate for non-potable.	Compliant with method requirements.
Section 4	NA	Added text for chlorine, nitrate and nitrite as interferences	Accurately describe laboratory practice.
Section 7	NA	Added cadmium carbonate and CN Complex Standard to reagent section.	Accurately describe laboratory practice.
Section 8	Paragraph format	Table format	Compliant with new SOP format recommendations.
Section 9	Paragraph format	Table format	Compliant with new SOP format recommendations.
Section 10	NA	Added Complex Standard and clarified QC prep.	Accurately describe laboratory practice.
Section 10.5	NA	Example Analysis Queue added.	Compliant with new SOP format recommendations.

Section	Change from	Change to	Reason
Section 13	Section 13 – Waste Management and Pollution Control	Section 13 separated into two sections: Section 13 – Pollution Control and Section 14 – Waste Management	Compliant with new SOP format recommendations.
Section 14	In an acceptable manner	In accordance with all federal and state laws and regulations.	Consistency with other SOPs (VAP requested this statement)
Section 15	NA	Added other laboratory SOPs.	Compliant with new SOP format recommendations.

Table 1: Calibration Standard/ICV Preparation

Standard	Volume	Of Solution	Diluted with 0.25N NaOH to	= Concentration
Standard 1	15 mL	Calibration Working Std.	250 mL	300 ug/L
Standard 2/CCV	5 mL	Calibration Working Std.	250 mL	100 ug/L
Standard 3	10 mL	Standard #1	100 mL	30 ug/L
Standard 4	10 mL	Standard #2	100 mL	10 ug/L
Standard 5	5 mL	Standard #2	100 mL	5 ug/L
ICV	5 mL	ICV Working Standard	200 mL	125 ug/L
Complex LCS	1 mL	Complex Working Standard	50 mL	100 µg/L

Note: Calibration concentrations may be changed, however, a minimum of a five-point calibration is required. One of the concentrations must be at or below the reporting limit. If concentrations are changed, then the preparation must be modified accordingly. Standards are made fresh daily.

Table 2: Method Comparisons

Issue	Method	Comparison
Chlorinated samples	335.4	Test w/ KI test paper, treat w/ ascorbic acid crystals; **can use sodium arsenite.**
	SW9012B	Test w/ KI test paper, treat w/ 0.1N sodium arsenite; can use ascorbic acid crystals but not as effective.
	SM4500 CN B	**Test w/ KI test paper moistened w/ acetate buffer, treat w/ 0.1g sodium arsenite.**
Treatment for sulfides	335.4	Treat sulfides w/ cadmium carbonate.
	SW9012B	Treat sulfides w/ bismuth nitrate.
	SM4500 CN B	**Treat sulfides w/ lead carbonate.**
Amenable CN	335.1	Does not mention use of lamp.
	SW9012B	Perform under amber light.
	SM4500 CN G	**Perform under incandescent light w/ foil wrapped beakers.**
Distillation	335.4	**50mL sample in midi-distillation w/ appropriately reduced amount of reagents.**
	SW9012B	500mL sample in macro-distillation.
	SM4500 CN C	500mL sample in macro-distillation.
Chloramine-T	335.4	2g to 500mL.
	SW9012B	2g to 500mL and refrigerate until ready to use.
	SM4500 CN E	**1g to 100mL, refrigerate and prepare weekly.**
Buffer Solution	335.4	**Specifies a phosphate buffer.**
	SW9012B	Does not specify a specific buffer.
	SM4500 CN E	Specifies an acetate buffer.
Standards	335.4	**Titrate stock standard w/ $AgNO_3$ after makeup/receipt.**
	SW9012B	Does not specify treatment of stock standards.
	SM4500 CN E	Titrate stock standard w/ $AgNO_3$ after makeup/receipt and check weekly.
Dilution Solution	335.4	**Specifies a 0.25N for distillations and standards**.
	SW9012B	Specifies a 0.25N for distillations and .02N for standards.
	SM4500 CN E	Specifies a 0.04N for distillations and standards.
Curve Analysis	335.4	**Analyze in order of decreasing concentration.**
	SW9012B	Analyze in order of increasing concentration.
	SM4500 CN C	Does not specify.

Title: Method 608 – Organochlorine Pesticides and PCBs by Gas Chromatography

Approvals (Signature/Date):

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1.0 Scope and Application

1.1 Method 608, as directed in this SOP, is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs) in hexane extracts prepared from various types of solid and liquid wastes, soils, and water municipal and industrial discharges.

1.2 Non-Aqueous Samples are prepared using Pressurized Fluid Extraction (SW 3545)/DT-ORG-018 and/or Waste Dilution (SW 3580A)/DT-ORG-024. Aqueous samples are prepared using Separatory Funnel (SW 3510)/DT-ORG-019. **Continuous Liquid/ Liquid extraction is not acceptable for this procedure (2009 NELAC audit)**

1.3 Please see the LIMS for the current default reporting limits. Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory-specific method detection limit (MDL) data, project specific DQOs, regulatory requirements are all taken into account, as well as instrument-to-instrument repeatability.

1.4 This method by Gas Chromatography describes analytical conditions for a second gas chromatographic column that can be used to confirm identifications made with the primary column.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph and skilled in the interpretation of chromatograms produced by such a system. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.6 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis with the supporting demonstration as indicated in the QA Manual.

2.0 Summary of Method

2.1 A measured portion of sample, approximately 1 L for waters or approximately 10g for soils, is extracted with methylene chloride. The extract is dried and exchanged to hexane during concentration to a volume of 10 ml or less. The extract is separated by gas chromatography and the parameters are then measured with an electron capture detector.

2.2 The method provides an elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

3.0 Definitions

3.1 Primary and Secondary Column - The primary column refers to the column which is used for quantitation. The secondary column is used for qualification only. Either column can be used for quantitation and reporting if it meets the acceptance criteria.

3.2 Extraction batch - Environmental samples which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 10 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours.

3.3 Aroclor - The trade name for mixtures containing PCBs. Since each Aroclor is a mixture, they may be described as multicomponent analytes. Aroclors may contain compounds in addition to PCBs but the term PCBs and Aroclors are commonly used interchangeably. The names of the Aroclor mixtures, such as 1242 and 1260, refer to the 12 member

biphenyl ring and the percent chlorinated by weight.

3.4 Muticomponent Analyte - A chromatograph of a multicomponent analyte will contain several peaks. All Aroclors evaluated by this procedure are mult-component analytes. Some of the pesticides evaluated (Toxaphene & Technical Chlordane) are also multi-component analytes.

3.5 DCB - The surrogate Decachlorobiphenyl

3.6 TCX - The surrogate Tetrachlorometaxylene

4.0 Interferences

4.1 Sources of interference in this method can be grouped into three broad categories.

4.1.1 Contaminated solvents, reagents or sample processing hardware.

4.1.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

4.1.3 Compounds extracted form the sample matrix to which the detector will respond.

- Interferences co-extracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

4.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. This interference can best be minimized by avoiding contact with plastic materials and checking all solvents and reagents for phthalate contamination. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

4.3 Glassware must be scrupulously cleaned. Extraction glassware is detergent washed with hot water and rinsed with tap water and organic-free reagent water. This is followed by methylene chloride and methanol rinses.

4.4 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. Activated copper is suggested for removal of sulfur.

4.5 PCBs may interfere with the analysis of pesticides, particularly the multicomponent analytes such as Chlordane or Toxaphene.

4.6 Co-elution among the many target analytes in this method can cause interference problems.

4.7 Poor GC performance may be expected when a chromatographic system is contaminated with high-boiling point materials, particularly in the injector. Routine maintenance should be performed such as replacement of septa, metal seals, liners and removing as much as 0.5 – 1 M from the injector side of the capillary column.

4.8 Carrier gas should be scrubbed to remove traces of oxygen and scrubbers should be changed regularly. Carrier gas must always be passed through the column whenever the oven is heated.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) 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

The task of crimping vials could involve repetitive motions which could cause stress and an illness for the employee. Employees must avoid carrying out these tasks for extended periods of time and the work must be split up among the employees where possible.

The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

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 standards 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
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Sylon- CT 5% in Toluene	Flammable Carcinogen Teratogen Reproductive hazard Severe eye irritant Skin irritant	Toluene 200 ppm PEL 200 ppm TWA Ceiling 500 Maximum	May cause respiratory track irritation. Vapors may cause drowsiness or dizziness. Exposure to the eyes will cause sever irritation.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Gas chromatograph: an analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, autosamplers, electron capture detectors (ECD), and data system. It is recommended that the system be equipped with two ECDs. The Agilent Technologies Model 5890 or 6890 is preferred.

The data acquisition system must be capable of time stamping all data produced with the correct date and time. If calibration curves are to be used in place of average response factor calibration, the system must be capable of plotting the curves and calculating correlation coefficients.

6.2 GC columns. The following pair of columns is used:

6.2.1 Restek Rtx-CLPesticides 30m, 0.32mm ID, 0.50um (Cat. #11139) or equivalent and

6.2.2 Restek Rtx-CLPesticides2 30m, 0.32mm ID, 0.25um (Cat. #11324) or equivalent

6.3 Hamilton or Agilent Technologies 5 uL or 10 uL autosampler syringes.

6.4 Restek Siltek single gooseneck injection port liners.

6.5 Restek Ice Blue Injection port septa.

6.6 Restek injection port gold seals.

6.7 Class A Volumetric flasks of varying concentrations for preparation of standards.

6.8 Microsyringes of varying volumes for preparation of standards and dilution of samples.

6.9 Amber 2 mL crimp top

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

7.1 All stock standard solutions must be replaced six months after opening, or sooner if routine QC tests indicate a problem. All other standard solutions, dilutions or mixtures, must be replaced after six months or sooner if routine QC indicates a problem. All standards must be stored at <6.0^{o} C but not frozen.

7.2 Organic-free reagent water.

7.3 All solvents must be stored at room temperature in appropriate storage area.

7.3.1 n-Hexane, pesticide grade or better.

7.3.2 Acetone, pesticide grade or better.

7.3.3 Methylene chloride, pesticide grade or better.

7.3.4 Methanol, reagent grade or pesticide grade.

7.4 Calibration standards. See Tables 1a, 1b, 2a, 2b, 2c, 3 & 4.

7.5 ICV Standard. See Tables 1a & 1b for Standard source. This standard is prepared from a source separate from the calibration standards. The ICV is prepared from the same source as the LCS, but not necessarily at the same concentrations.

7.6 Supelco Sylon CT 5% for silanization of standards glassware.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

8.2 Sampling equipment must be as free as possible from Tygon tubing and other potential sources of contamination.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Aqueous	Amber Glass	1 L	Cool <6.0°C, but not frozen. Reduce residual chlorine using 80 mg sodium thiosulfate per 1L of sample.	Pesticides: 7 days from collection to extraction PCBs: 1 year from collection to extraction	SW-846 Chapter 4, CFR
Non-Aqueous	8oz glass	50g	Cool<6.0°C, but not frozen.	Pesticides: 14 days from collection to extraction PCBs: 1 year from collection to extraction	SW-846 Chapter 4, CFR
Extracts	2mL amber autosampler vials	N/A	Protect from light. Store –10°C to –20°C in sealed vials with un-pierced PTFE-lined septa.	Pesticides: 40 days from extraction to analysis PCBs: 1 year from extraction to analysis	SW-846 Chapter 4, CFR

9.0 Quality Control

9.1 The following quality control samples are prepared.

Preparation QC

Quality Controls	Frequency	Comments
Method Blank (MB)	1 per preparation batch[1]	For soils, use sand as the matrix. For waters, used DI water as the matrix.
Laboratory Control Sample (LCS)	1 per preparation batch[1]	For soils, use sand as the matrix. For waters, used DI water as the matrix.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)[2]	1 per preparation batch[1]	If there is insufficient sample for an MS/MSD, note this on the bench-sheet , along with the reason.
Surrogates	Each standard and sample	Corrective action required if both are unacceptable.

[1]Preparation batch is limited to 20 samples
[2]The sample selection for MS/MSD is random, unless specifically requested by a client.

9.2 If an extract cleanup procedure was performed, refer to the appropriate cleanup SOP for quality control procedures.

9.3 Run Batch - is initiated with the injection of the first calibration standard or CCV. The batch may include as many injections as can be made within 24 hours of the injection of the CCV. A closing CCV is not required for method 608. Any sample analyzed outside the 24-hour clock must be re-analyzed.

9.4 Retention time windows - The retention time windows are established initially by injection of three calibration standards over 72 hours. The mean and standard deviation of the retention times are calculated. A retention time window is established as ± 3 Standard Deviations from the mean retention time. The absolute retention time window must be established for each Aroclor peak and surrogate on each column and instrument. New retention time windows must be established when new columns types are installed.

9.5 Method Blank – A method blank must be included with every extraction batch but not necessarily every instrument run batch.

9.5.1 Typically, the method blank is analyzed prior to sample analysis to insure the chromatographic system is contaminant-free.

9.5.2 When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the method blank associated with those samples (e.g., extracted with the samples) must be analyzed on at least one of those instruments.

9.5.3 Acceptance criteria is <RL. If the method blank shows a detection above the required reporting limit, it must be reanalyzed. If this fails to correct the problem, all associated samples with concentrations above the reporting limit, for that analyte, must be re-extracted.

- If the associated samples are non-detect, then reanalysis of the Method Blank is not required and re-extraction of samples is not required.
- If the concentration found in the samples is >10X the concentration found in the Method Blank, reanalysis is not required, but data must be flagged.
- The laboratory must not subtract results of the method blank from those of any associated samples. Such “blank subtraction” is inappropriate.

- Method blanks may be used to check contamination by carryover from a high-concentration sample into subsequent samples. If the analytes in the high-concentration sample are not present in the subsequent blank, then lack of carryover has been demonstrated.

9.6 Laboratory Control Standard (LCS) – A LCS is extracted with every batch. If the LCS is unacceptable, all samples extracted with the failed LCS must be re-extracted and re-analyzed. The LCS spike is from a different source than the calibration standards.

9.6.1 Acceptance limits are based on method 608 Table 3. Those limits not available in the method (for example, Endrin Aldehyde) are generated based on historic data. All control limits are maintained in the LIMS.

9.6.2 If the LCS recovery is high, and the associated samples are <RL, corrective action is not necessary, but data must be flagged.

9.6.3 Separate LCS spikes are used for PCBs and Pesticides.

9.6.4 The PCB spike contains Aroclors 1016 and 1260 and the Pesticide spike contains the single component pesticides of interest. This mix does not include Chlordane or Toxaphene.

- The PCB or Pesticide used for the LCS may be modified to meet client or other needs. For example, if samples are being analyzed only for PCB 1242, it may be appropriate to spike the LCS with this analyte.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – When adequate sample is provided, a set of client samples are spiked with the LCS spike described above to demonstrate any matrix interferences.

9.7.1 Acceptance limits are based on method 608 Table 3. Those limits not available in the method (for example, Endrin Aldehyde) are generated based on historic data. Control limits are maintained in the LIMS.

9.7.2 If the MS/MSD does not pass acceptance criteria, the parent and MS/MSD must be flagged. The MS/MSD is not used for batch control.

9.8 Surrogates. All samples and standards will be spiked with two surrogates, DCB & TCX.

9.8.1 Surrogate limits are generated based on historic data, and are maintained in the QA Manual & programmed into LIMS.

9.8.2 Any sample, including batch QC, with surrogates outside the control limits requires evaluation by the laboratory. Once the problem has been identified and addressed, corrective action may include the reanalysis of samples, or the extraction and analysis of new sample aliquots.

9.8.3 If the blank, LCS or individual sample surrogate recoveries are high, and the associated analytes are non-detect, then reanalysis and/or re-extraction is not necessary, but the data must be flagged.

9.8.4 If one of the two surrogates is passing, corrective action is not required.

9.9 Manual integrations

9.9.1 All manual integration of standards, samples and extraction batch QC must be clearly documented. The raw data must include a copy of the manual integration that is dated and signed by the analyst performing the integration. It must also include an explanation as to why the integration was performed. For more details on manual integrations, see the manual integration SOP.

10.0 Procedure

10.1 Sample extraction – Refer to Extraction SOPs for guidance in choosing the appropriate extraction procedure.

10.2 Extract cleanup – Cleanup procedures may not be necessary for a relatively clean sample matrix, but some extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements.

10.2.1 Elemental sulfur, which may be present in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in Method 3660. This Copper clean up is generally used when there are broad peaks that cover a wide area, especially the first half of the chromatogram.

10.3 GC Conditions

10.3.1 Single-column analysis with the use of two narrow bore capillary columns each attached to separate injector systems may be used. Alternatively, a system with a single injector split to dual columns may be used.

10.3.2 Table 6a & 6b lists the GC operating conditions.

10.3.3 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day or more. Therefore the GC column should be primed (or deactivated) by injecting a pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

10.4 Calibration

The Initial Calibration involves the analysis of standards containing the target compounds at a minimum of three different concentrations. The Initial calibration establishes the working range of the system. The lowest level must be at, or below, the Reporting Limit. The extrapolation of the calibration to concentrations above the actual calibration is not appropriate.

10.4.1 A typical calibration for Pesticides includes all the single component pesticides as well as single points for Toxaphene and Chlordane.

- Separate calibrations for Toxaphene and Chlordane are run only when the presence of either compound is suspected, based on comparison with the single point standards.

10.4.2 A typical calibration for PCBs includes 1016/1260, as well as single points for 1221, 1232, 1242, 1248, 1254, 1262 & 1268.

- Separate calibrations for 1221, 1232, 1242, 1248 & 1254 are run only when the presence of these Aroclors is suspected, based on comparison with the single point standards.
- Aroclors 1262 & 1268 are for Identification purposes only. If these are detected in samples they are quantified against 1260 and narrated.

10.4.3 Analyze a minimum of three calibration standards. For PCBs select a minimum of 3 characteristic peaks each Aroclor. Peaks should be at least 25% of the height of the largest Aroclor peak.

10.4.4 Calculate the response factor (RF) for each single component pesticide, and for each characteristic Aroclor peak at each concentration level.

10.4.5 If the RSD of the calibration levels is less than or equal to 10%, then the response of the instrument is considered linear and the mean or average response factor can be used to quantitate sample results. For PCBs, the mean RSD is evaluated against this criteria.

- When the Aroclor 1016/1260 mixture is used to demonstrate the detector response, the calibration model (RF or linear regression) chosen for this mixture must be applied to the other five Aroclors for which single standards were analyzed.

10.4.6 Alternatively, a least squares regression may be utilized and the correlation coefficient (r) must be greater than or equal to 0.99. (Enviroquant measures r^2 which must be greater than or equal to 0.980).

10.4.7 Initial calibration curves must be re-run each time the CCV criteria is not met and each time a significant change to the analytical system is made. (A significant change would include installation of new columns or detectors or change in temperature program but would not include the changes made from daily maintenance such as replacing a septa or liner or trimming of the analytical column.)

10.4.8 If the initial calibration curve fails to meet the 10% RSD criterion or the, >0.99 linear regression criterion, that analyte cannot be reported on that column. If the curve fails on both columns for any analyte, corrective action becomes necessary. Suggested corrective actions include injector/column maintenance , preparation of new calibration standards, installation of new columns and/or refurbishment of the ECD detectors.

10.4.9 A calibration is required for the compounds of interest only. It is not necessary to provide a pesticide calibration when reporting PCBs only.

10.5 Initial Calibration Verification Standard (ICV) – A standard from a source independent of the calibration standards is analyzed following every initial calibration curve. The quantitated results of the ICV must be within ± 30% of the true concentration of each analyte and surrogate in the ICV. The ICV may be used as a CCV but must meet the more strict criteria outlined in 10.6.

10.6 Continuing Calibration Verification (CCV) – Verify the calibration daily by injecting a CCV prior to conducting any sample analyses. A CCV is required for both Pesticides and PCBs, if both are targets. A CCV must be injected at intervals of at least every 24 hrs. For method 608, a CCV is not required at the end of the sequence.

10.6.1 The mean Response Factor for each analyte (expressed as the aggregate of the peaks used for quantitation) must not exceed a ± 15% difference (± 30% for surrogates) from the mean Response Factor calculated for the initial calibration. When using regression, the % Drift must not exceed ±15% (± 30% for surrogates) of the true value. See Section 11 for the calculations.

10.6.2 When a CCV fails to meet the QC criteria, all samples that were injected after the last CCV that passed must be re-injected.

- If the failed analytes are not targets for the associated samples, then results can be reported without qualification.
- If the CCV exhibits a response for an analyte that is above the acceptance limit (>115% recovery) and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not

need to be reanalyzed and may be reported without qualifiers, although data must be clearly annotated.

10.6.3 Verify Retention times for each analyte and surrogate with each CCV. New midpoints for the windows may be set with each CCV. (Daily maintenance of the GC may include removing a portion the column. This action may result in a shift of retention times).

10.7 Sample Analysis

10.7.1 Samples and Extraction batch QC may be analyzed following successful calibration verification. Generally it is advisable to analyze the extraction method blank and LCS prior to sample analysis. A post CCV is not required.

10.7.2 Proper quantitation requires the appropriate selection of a baseline from which the peak area can be determined.

10.7.3 If the response for a target analyte exceeds the calibration range of the system, dilute the extract and re-analyze.

10.7.4 Identification of Aroclors and of Toxaphene and Chlordane is based on the characteristic “fingerprint” retention time and shape of the indicator peaks. Quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peaks of the same retention time and shape generated using an external calibration procedure. Alternatively, peak heights may be used.

10.7.5 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. In these cases, quantitation will be performed on the basis of the Aroclor standard that is most similar to the sample.

10.7.6 When using the external calibration procedure, determine the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. Proper quantitation requires the appropriate selection of a baseline from which the peak area or height can be determined.

10.7.7 Qualitative confirmation is required for reported hits in samples. This can be accomplished via second column GC analysis.

- For second column analysis for PCBs, conduct a qualitative comparison of the chromatographic pattern from the sample to that of a reference chromatogram (may be based on a single point calibration standard). If the second column confirms the identity of the PCB, then report the results from the Primary column without qualification.
- For second column analysis for pesticides, evaluate peaks in the retention time window on the second column (may be based on a single point calibration standard) to determine if a tentative hit on the primary column is confirmed.
- When samples are analyzed from a source known to contain specific analytes, the results may not require 2nd column confirmation. This approach should not be attempted for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors. In order to employ this approach, the analyst must document the source-specific information indicating what Aroclors are anticipated in the sample (historical data, generator knowledge…)

10.8 PCB Screens

10.8.1 Prep QC- Method Blank only

10.8.2 Analytical QC- Same as non screens

11.0 Calculations / Data Reduction

11.1 Response factors (RF) = $\frac{\text{Total Area Response within RT window}}{\text{Concentration of Standard}}$

11.2 Relative Standard Deviation (%RSD) = $\frac{SD}{RF_{ave}} \times 100$

where:

RF_{ave} = The average of the 5 or more initial calibration RFs

SD = The standard deviation of the average RFs

11.3 Linear Regression Calculation - This calculation is used when the %RSD exceeds 20%.

$$y = ax + b$$

where:

y = Instrument response (total area sum)

a = Slope of the line (coefficient of x)

x = Concentration of calibration standard

b = The intercept

The Enviroquant data system is capable of generating a linear plot. The analyst should not force the line through the origin.

11.4 Percent Difference (%D) = $\frac{|RF_{av} - RF_{c}|}{RF_{ave}} \times 100$

where:

RFav = The average of the 5 or more initial calibration RFs

RFc = Continuing calibration RF

11.5 Extract (raw) concentration- using average curve fit

$$\textbf{Conc (µg/L)} = \frac{(A_{xc})}{(RF_{ave})}$$

where:

A_{xc} = Area response
RF_{ave} = Average RF from initial calibration

11.6 Extract (raw) concentration- using linear regression.

$$Conc_{RAW} = \frac{A_T - b}{a}$$

Where:

A_T = Area of sample peak
b = The intercept
a = Slope of the line (coefficient of x)

11.7 Concentration in Aqueous samples:

$$\textbf{Conc. (µg/L)} = \frac{(C_r)(DF)}{(Vi)}(Vf)$$

Where:

C_r = Concentration reported by the data system in µg/mL.
Vi = Initial volume of sample
Vf = Final volume of extract
DF = Dilution factor

11.8 Concentration in Soil/Sediment samples:

$$\textbf{Conc. (µg/Kg)} = \frac{(C_r)(DF)}{(W_s)(S)}$$

Where: C_r = Concentration reported by the data system in µg/L.
W_s = Wet Weight of sample extracted, grams
S = Solid fraction, % solids/100 , optional

11.9 Matrix Spike/Matrix Spike Duplicate Percent Recovery or LCS Percent Recovery:

$$\%Recovery = \frac{C - C_X}{(C_{SP})} \times 100$$

where:

C = Concentration of Aroclor in Matrix Spike, Matrix Spike Duplicate, or LCS

C_X = Concentration of Aroclor in unspiked sample

C_{sp} = Spike level.

This formula is used to calculate LCS recoveries as well. $C_x = 0$ in the LCS.

11.10 Relative Percent Difference (RPD) of Matrix Spikes =

$$RPD = \frac{(\text{Larger value} - \text{Smaller Value})}{(\text{Sum of the values}/2)} \times 100$$

11.11 Surrogate % Recovery = $\frac{\text{Concentration detected}}{\text{Concentration spiked}} \times 100$

12.0 Method Performance

12.1 Demonstration of Capabilities - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.2 Method Detection Limit Study - A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 The supervisor has responsibility to ensure that an analyst who has been performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

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 accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.1 The following waste streams are produced when this method is carried out:

- Acidic waste generated in the lab is neutralized and discharged into the sanitary sewer.
- Solvent waste generated by the extraction is collected, drummed and disposed of through a Waste Handler.
- Expired primary and working PCB standards >50ppm are collected, drummed and disposed of through a Waste Handler.
- Vials containing sample extracts are treated as solvent waste.

15.0 References / Cross-References

40 CFR App A, Part 136, Method 608- Organochlorine Pesticides and PCBs

16.0 Method Modifications

None

17.0 Attachments

Table 1a	Pesticide Standard Sources
Table 1b	PCB Standard Sources
Table 2a	Preparation of Single Component Pesticides Calibration Standards
Table 2b	Preparation of Aroclors 1016/1260 Calibration Standards
Table 2c	Preparation of Aroclor 1242* Calibration Standards
Table 3	Preparation of Toxaphene Calibration Standards
Table 4	Preparation of Chlordane Calibration Standards
Table 5a	Estimated Pesticide Retention Times
Table 5b	Estimated PCB Retention Times
Table 6a	Example GC Operating Conditions for Pesticides
Table 6b	Example GC Operating Conditions for PCBs

18.0 Revision History

18.1 Revision dates

- 4/30/2010 Biennial review
- 4/30/2008 Original (replaces DT06-05 rev 11)

18.2 Changes from last revision

Section	Change from	Change to	Reason
Copyright	2008 information	2010 information	Updated corporate template.
1.2	Added	Non-Aqueous Samples are prepared using Pressurized Fluid Extraction (SW 3545)/DT-ORG-018 and/or Waste Dilution (SW 3580A)/DT-ORG-024. Aqueous samples are prepared using Separatory Funnel (SW 3510)/DT-ORG-019. **Continuous Liquid/ Liquid extraction is not acceptable for this procedure (2009 NELAC audit)**	Identify prep procedure and ensure that samples are not prepped using Continuous Liquid/Liquid extraction.
1.4	…to confirm measurements made	…to confirm identifications made	Confirmation for this test is for Identification, not for Quantification.
2.2	…a Florisil column cleanup procedure…	Removed	Florisil clean up is not currently performed at this facility.
3.2	Extraction batch – A set of up to 10 samples extracted by the same analyst(s) using the same techniques.	Extraction batch - Environmental samples which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 10 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours.	Provide definitions that are consistent with the Quality Assurance Manual.
6.2	J & W DB-5 30m, 0.32mm ID, 0.25um or DB-XLB, 30m, 0.32mm, 0.25 um or equivalent and J & W DB-35 30m, 0.32 mm ID, 0.25um or equivalent	Removed	These columns are not in use at this facility.
8	Paragraph form	Table form	Updated lab template.
9	Paragraph form	Table form	Updated lab template.
9.4	New retention time windows must be established when new columns are installed.	New retention time windows must be established when new columns types are installed.	Provide specific detail regarding when new Retention Time Windows are required.
10.2	Method 3620 (fluorisil) may be used to separate organochlorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds. Florisil is generally used when there is a “humpogram” in the later half of the chromatogram.	removed	Florisil clean up is not performed at this facility.

10.5	The quantitated results of the ICV must be within ± 30% of the true concentration of each analyte.	The quantitated results of the ICV must be within ± 30% of the true concentration of each analyte and surrogate	Provide specific information regarding the required evaluation of surrogates in the CCVs.
10.6	A CCV is required for both Pesticides and PCBs, if both are targets. A CCV must be injected at intervals of not less than once every 24 hrs. For method 608, a CCV is not required at the end of the sequence.	A CCV is required for both Pesticides and PCBs, if both are targets. A CCV must be injected at intervals of at least every 24 hrs. For method 608, a CCV is not required at the end of the sequence.	CCVs must be injected at least every 24 hrs. The original word was confusing.
10.6.1	…must not exceed a ± 15% difference from the mean Response Factor calculated for the initial calibration. When using regression, the % Drift must not exceed ±15% of the true value.	…must not exceed a ± 15% difference (± 30% for surrogates) from the mean Response Factor calculated for the initial calibration. When using regression, the % Drift must not exceed ±15% (± 30% for surrogates) of the true value.	Provide specific information regarding the required evaluation of surrogates in the CCVs.
10.6.2	…then the extracts for those samples do not need to be reanalyzed and may be reported with qualifiers.	…then the extracts for those samples do not need to be reanalyzed and may be reported without qualifiers, although data must be clearly annotated.	Clarify data qualifier requirements.
10.6.3	New windows may be set with each CCV.	New mid points for the windows may be set with each CCV.	Clarify procedure.
10.7.7	Second column confirmation is required for any detections in samples.	Qualitative confirmation is required for reported hits in samples. This can be accomplished via second column GC analysis.	Clarify that confirmation is for qualitative purposes only and will only be done when tentative hits are detected on the primary column.
10.7.7	The second column should meet the same initial calibration and daily verification criteria of the primary column. When the sample results are confirmed using two dissimilar columns, the agreement between the quantitative results should be evaluated after the identification has been confirmed.	removed	Confirmation of this test is being done for qualitative purposes. Full calibration for the confirmation is not required.
10.7.7	When the sample results are confirmed using two dissimilar columns, the agreement between the quantitative results must be evaluated after the identification has been confirmed.	removed	Confirmation for this test is being done for qualitative purposes. Full calibration for the confirmation is not required. Without full calibration, quantitation is not done so comparison between the primary and secondary results for quantitative purposes is not performed.

10.7.7	Calculate the relative percent difference (RPD) as described in Section 11. If one result is significantly higher (e.g. >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or operator) during peak integration.	removed	Confirmation for this test is being done for qualitative purposes. Full calibration for the confirmation is not required. Without full calibration, quantitation is not done so comparison between the primary and secondary results for quantitative purposes is not performed.
10.7.7	If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the higher result. The client must be advised of the disparity between the results on the two columns	removed	Confirmation for this test is being done for qualitative purposes. Full calibration for the confirmation is not required. Without full calibration, quantitation is not done so comparison between the primary and secondary results for quantitative purposes is not performed.
10.7.7	Added	For second column analysis for PCBs, conduct a qualitative comparison of the chromatographic pattern from the sample to that of a reference chromatogram (may be based on a single point calibration standard). If the second column confirms the identity of the PCB, then report the results from the Primary column without qualification. For second column analysis for pesticides, evaluate peaks in the retention time window on the second column (may be based on a single point calibration standard) to determine if a tentative hit on the primary column is confirmed.	Clarify procedure for confirmation- including that only single point standards are required for confirmation.
10.8	Added	PCB Screens Prep QC- Method Blank only Analytical QC- Same as non screens	Clarify procedure.
13	Waste Management and Pollution Control	Split into two sections	Consistency with updated laboratory SOP format.

Table 1a. Pesticide Standard Sources:

	Calibration Standards			*Verification Standards*		
Analyte	**Vendor/ Catalog #**	**Conc. (ug/mL)**	**Solvent**	**Vendor/ Catalog #**	**Conc. (ug/mL)**	**Solvent**
Aldrin	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
α-BHC	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
β-BHC	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
δ-BHC	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
γ-BHC (Lindane)	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
α-Chlordane	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
γ-Chlordane	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
4,4'-DDD	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
4,4'-DDE	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
4,4'-DDT	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
Dieldrin	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
Endosulfan I	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
Endosulfan II	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
Endosulfan sulfate	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
Endrin	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
Endrin aldehyde	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
Endrin ketone	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
Heptachlor	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
Heptachlor epoxide	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
4,4'-Methoxychlor	R-32291	200	Hexane	U-PPM-808C	1000	Hexane/Toluene
Multi-component Standards:						
Chlordane, Technical*	R-32021	1000	Hexane	S-4-8065	1000	Isooctane
Toxaphene *	R-32005	1000	Hexane	S-4-8103	1000	Isooctane
Surrogates:						
Decachlorobiphenyl	R-32000	200	Acetone	S-4-8460	200	Isooctane
Tetrachloro-m-xylene	R-32000	200	Acetone	S-4-8460	200	Isooctane
Breakdown Standard:						
4,4'-DDT/Endrin	S-4-8282	500	Acetone	Not applicable		

Table 1b. PCB Standard Sources:

	Calibration Standards			*Verification Standards*		
Analyte	**Vendor/ Catalog #**	**Conc. (µg/mL)**	**Solvent**	**Vendor/ Catalog #**	**Conc. (µg/mL)**	**Solvent**
Aroclor 1016	R-32006	1000	Hexane	A-90123	1000	Hexane
Aroclor 1221	R-32007	1000	Hexane	A-90124	1000	Hexane
Aroclor 1232	R-32008	1000	Hexane	A-90125	1000	Hexane
Aroclor 1242	R-32009	1000	Hexane	A-90126	1000	Hexane
Aroclor 1248	R-32010	1000	Hexane	A-90127	1000	Hexane
Aroclor 1254	R-32011	1000	Hexane	A-90128	1000	Hexane
Aroclor 1260	R-32012	1000	Hexane	A-90129	1000	Hexane
Surrogates:						
Decachlorobiphenyl	R-32000	200	Acetone	S-4-8460	200	Isooctane
Tetrachloro-m-xylene	R-32000	200	Acetone	S-4-8460	200	Isooctane

S=Supelco,R=Restek,A=Absolute Standards

Table 2a. Preparation of Single Component Pesticide Calibration Standards:

Cal. Standard	**Pesticide Conc. (µg/L)**	**Surrogate Conc. (µg/L)**	**Cal. Stock in 100 mL (µL)**	**Surr. Stock in 100 mL (µL)**
CAL 1	10	2	5	1
CAL 2	20	4	10	2
CAL 3	50	10	25	5
CAL 4	80	16	40	8
CAL 5	100	20	50	10
CAL 6	160	40	80	20
ICV	50	10	50	5

Table 2b. Preparation of Aroclors 1016/1260 Calibration Standards:

Cal. Standard	**Ar 1016 Conc. (µg/L)**	**Ar 1260 Conc. (µg/L)**	**Surrogate Conc. (µg/L)**	**Cal. Stock 1016 in 100 mL (µL)**	**Cal. Stock 1260 in 100 mL (µL)**	**Surr. Stock in 100 mL (µL)**
CAL 1	20	20	4	2	2	2
CAL 2	50	50	10	5	5	5
CAL 3	100	100	20	10	10	10
CAL 4	150	150	30	15	15	15
CAL 5	200	200	40	20	20	20
ICV	100	100	20	10	10	10

Table 2c. Preparation of Aroclor 1242 Calibration Standards:

Cal. Standard	Aroclor Conc. (µg/L)	Surrogate Conc. (µg/L)	Cal. Stock in 100 mL(µL)	Surr. Stock in 100 mL(µL)
CAL 1	20	4	2	2
CAL 2	50	10	5	5
CAL 3	100	20	10	10
CAL 4	150	30	15	15
CAL 5	200	40	20	20
ICV	100	15	10	7.5

* Note: Aroclor 1221, 1254, 1232, or 1248 can be substituted for 1242.

Table 3. Preparation of Toxaphene Calibration Standards:

Cal. Standard	Toxaphene Conc. (µg/L)	Surrogate Conc. (µg/L)	Cal. Stock (1000 µg/mL) in 100 mL (µL)	Surr. Stock (200 µg/mL) in 50 mL (µL)
CAL 1	20	2	1	1
CAL 2	50	5	2.5	2.5
CAL 3	100	10	5	5
CAL 4	200	20	10	10
CAL 5	400	40	20	20
ICV	100	20	5	10

Table 4. Preparation of Chlordane Calibration Standards:

Cal. Standard	Chlordane Conc. (µg/L)	Surrogate Conc. (µg/L)	Cal. Stock (1000 µg/mL) in 50 mL (µL)	Surr. Stock (200 µg/mL) in 50 mL (µL)
CAL 1	20	2	5	1
CAL 2	50	5	10	2.5
CAL 3	100	10	15	5
CAL 4	200	20	20	10
CAL 5	400	40	25	20
ICV	100	20	15	10

Table 5: Estimated Pesticide Retention Times

	Rtx-CLPesticides (minutes)	**Rtx-CLPesticides2 (minutes)**
Aldrin	6.78	6.78
α-BHC	5.40	5.41
β-BHC	5.91	5.96
δ-BHC	6.13	6.32
γ-BHC (Lindane)	5.79	5.84
Chlordane, Technical*	MP	MP
α-Chlordane	7.98	8.04
γ-Chlordane	7.79	7.83
4,4'-DDD	9.00	9.19
4,4'-DDE	8.13	8.33
4,4'-DDT	9.41	9.65
Dieldrin	8.51	8.51
Endosulfan I	8.16	8.11
Endosulfan II	9.18	9.27
Endosulfan sulfate	10.50	10.23
Endrin	8.84	8.94
Endrin aldehyde	9.82	9.80
Endrin ketone	10.91	11.04
Heptachlor	6.40	6.38
Heptachlor epoxide	7.62	7.57
Hexachlorobenzene	5.18	5.21
Methoxychlor	10.20	10.78
Toxaphene *	MP	MP

*Multi-component mixtures

Table 6a: Example GC Operating Conditions- Pesticides

Carrier gas	Hydrogen
Carrier gas flow rate	52 cm/sec
Makeup gas	Nitrogen
Makeup gas flow rate	70 cm/sec
Injector temperature	200 ^{o}C
Detector temperature	325 ^{o}C
Initial temperature	120 ^{o}C
Initial time	1 min
Temperature program	120 ^{o}C to 200 ^{o}C @20 ^{o}/min, 200 to 300 ^{o}C @ 10 ^{o}C/min Hold at 300 ^{o}C for 2 min.
Final temperature	200 ^{o}C
Injection volume	1 µL
EPC:	
Constant Flow	On
Initial Pressure	7.5 psi
Purge Valve On Time	0.75 min

Table 6b. Example Operating Conditions- PCBs Using Rtx-CLPesticides/Rtx-CLPesticides2 Columns

Carrier gas	Hydrogen
Carrier gas flow rate	
Makeup gas	
Makeup gas flow rate	70 cm/sec
Injector temperature	200 ^{o}C
Detector temperature	300 ^{o}C
Initial temperature	120 ^{o}C
Initial time	0 min
Temperature program	
Final temperature	200 ^{o}C
Injection volume	1 µL
EPC:	
Constant Flow	On
Constant Flow Pressure	6 psi
Initial Pressure	7.5 psi
Purge Valve On Time	0.5 min

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Dayton
SOP Change Form
DT-QA-WI-017.1
Effective 7/2/09

SEE AMENDMENT AT FRONT OF DOCUMENT

NOTE: This form is not for use with OVAP SOPs. If changes are required a full revision is required.

SOP # with Revision DT-ORG-003.2

Title: Toxicity Characteristic Leaching Procedure (TCLP)/Synthetic Precipitation Leaching Procedure (SPLP)/Zero Headspace Extraction Procedure (ZHE)

Effective Date of Amendment: **11/10/11**

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COPY # :

ISSUED TO :

Revision Number with Mod ID: _____

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. ***Append this form to the front of the SOP copy.***

1. Briefly explain the reason for the update.

Change target weight for ZHE from 25g to 20-23g.

2. Category for SOP Change:

☐ Typographical Corrections (Non-Technical) – Retraining Not Required.

☐ Typographical Corrections (Technical- define below) – Retraining is required.

☒ Procedural Changes (Define Below) – Retraining Required.

3. Summary of Procedure Change (circle to indicate if there are attachments to this form: No / Yes: # pages attached = ___)

10.5.1 Add **The laboratory has set a maximum sample weight of 23 grams.**

10.5.6 If the waste is 100% solid, weigh out a ~~25~~-**20 – 23** gram subsample of the waste and record weight.

Does this change result in a Method Modification? Yes No **Method 1311 rev0 July 1992 section 7.3.3 clearly indicates a maximum weight of 25gram.**

If yes, please explain below. modification section of SOP must be corrected upon full revision.

11/10/11
Approval Signature/Date: Department Manager

Vicent Da 11/10/11
Approval Signature/Date: QA Manager or Designee

SEE AMENDMENT AT FRONT OF DOCUMENT

Title: Toxicity Characteristic Leaching Procedure (TCLP)/Synthetic Precipitation Leaching Procedure (SPLP)/Zero Headspace Extraction Procedure (ZHE)

USEPA SW-846 Method 1311, Rev. 0, July 1992;
USEPA SW-846 Method 1312, Rev. 0, September 1994

Approvals (Signature/Date):

Josh McKinney Department Manager 01/04/11 Date	Jason Lykins EH&S Officer 01/04/11 Date
Violet Fanning Quality Assurance Manager 01/04/11 Date	Tara Schlenker Laboratory Director 01/04/11 Date

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1.0 Scope and Application

1.1 The Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) are preparation procedures used to determine the mobility of both organic and inorganic analytes that may be present in a variety of wastes. These wastes may be liquid, solid, or multi-phasic.

1.2 In place of a TCLP/SPLP extraction and analysis, a total analysis may be used to demonstrate that individual analytes are not present or are present but below the specified regulatory levels.

1.3 If any analyte in a TCLP/SPLP fraction is determined to be greater than the regulatory limit the waste is considered to be hazardous.

1.4 This procedure contains procedures for both bottle extractors and zero headspace extractors (ZHEs). The ZHE must be used when extracting waste for volatile analysis.

1.5 This procedure can be used to prepare waste for analysis as described in the Ohio Administrative Code (OAC) 3745-30-03. This section of the code allows for extraction using an alternative extraction fluid as described in the American Society for Testing of Materials (ASTM) Method D 3987-85. The client should determine selection of this extraction fluid. The extraction fluid used in the initial characterization of a waste must be used for subsequent characterizations of a waste.

1.6 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis with the supporting demonstration as indicated in the QA Manual.

2.0 Summary of Method

2.1 For liquid wastes (less than 0.5% dry solid material) the waste, after filtration through a 0.6-0.8 micron glass fiber filter, is defined as the TCLP/SPLP extract.

2.2 For wastes containing greater than or equal to 0.5% dry solid material, the liquid, if any, is separated from the solid phase and stored for later analysis. The solid phase, if necessary, is reduced in particle size. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. A special extractor vessel is used when testing for volatile contaminants. Following extraction, the liquid extract is separated from the solid phase by filtration through a glass fiber filter.

2.3 If compatible, the initial liquid phase is added to the TCLP/SPLP extract, and after proper preservation, is ready for analysis. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 Definitions

3.1 Ceiling**:** concentration of a chemical that must not be exceeded.

3.2 Fluid Blank: a fluid blank is the blank leaching fluid used to extract the samples.

3.3 Matrix Spike (MS): field sample to which a known amount of target analyte(s) is added. Used to assess the effect of the matrix on the accuracy of the method. In TCLP/SPLP/ZHE analysis, the MS is spiked after leaching, and before analytical preparation procedures.

3.4 Matrix Spike Duplicate (MSD): a replicate matrix spike. Used to assess the effect of the matrix on the precision of the method. In TCLP/SPLP/ZHE analysis, the MSD is optional, and may be prepared if needed for other samples in the preparation batch. The MSD is spiked after leaching, and before analytical preparation procedures.

SEE AMENDMENT AT FRONT OF DOCUMENT

3.5 Percent solids: the fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure over a period of time, normally 15-30 minutes.

3.6 Please see the glossary in TestAmerica Dayton's Quality Assurance Manual (Document number DT-QAM-001) for additional definitions.

4.0 Interferences

4.1 Please see the individual analytical SOPs for method specific interference that may impact the results.

4.2 If samples are multi-phasic, the client should be consulted to determine if separate analyses are requested on each layer.

4.3 Note that for Oily wastes, a TCLP leach may not be required:

Memorandum #35 issued by Gail Hansen, Chief – Methods Section (OS-331) on June 12, 1992 states the following:

"To solve this problem, the Agency recommends a conservative approach, one that probably will overestimate the amount of leaching. Rather than performing the TCLP/SPLP extraction of the unfiltered portion of the oily waste, assume the waste is 100% liquid (e.g., will pass through the glass fiber filter) and perform a totals analysis on the oily waste to determine if the oil exceeds the appropriate regulatory level."

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) 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

5.1.1 Nitrile gloves should be used when performing this extraction. Latex and vinyl gloves provide no significant protection against organic solvents.

5.1.2 The rotary extraction device should be checked daily before use.

5.1.3 The use of a vacuum system during sample filtration presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed or marred in any manner must not be used under vacuum. It must be removed from service and replaced. Ensure that the vacuum exhaust hose is vented to a fume hood so vapors are not pumped into the working environment.

5.1.4 Pressure may build up in the extraction vessel. Vent into a hood if needed.

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

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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
Glacial 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.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 PPM-TWA 4 PPM-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.

1 – Always add acid to water to prevent violent reactions.

2 – Exposure limit refers to the OSHA regulatory exposure limit.

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6.0 Equipment and Supplies

6.1 The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and quality control requirements in this SOP can be met.

6.2 Agitator: Must be capable of rotating an extraction vessel in an end over end fashion at 30 ± 2 rpm.

6.3 Bottle Extraction vessel: When the waste is being tested for non-volatiles, a jar with sufficient capacity to hold the sample and the extraction fluid (20 times the weight of the sample) is needed. If the waste is being tested for metals only, a plastic container is acceptable. If the waste is being analyzed for organics, a glass container or fluorocarbon lined plastic container must be used.

6.4 Filtration Apparatus, non-volatile: Any filter holder capable of supporting a glass fiber filter. It is recommended that the apparatus have a minimum filter size of 11.0 cm and an internal capacity of 1.5 L. Filter devices must be of positive pressure and capable of generating 50 psi.

6.5 Minimum/Maximum Thermometer.

6.6 pH meter: The meter should be accurate within ± 0.05 units at 25° C.

6.7 Balance: The balance should be accurate within ± 0.1 grams.

6.8 9.5 mm (0.375 inch) sieve for particle size confirmation.

6.9 Hot plate capable of heating to 50°C. The hotplate is used for heating waste samples during pH determination.

6.10 Thermometer used for measuring temperature during the determination of pH of waste samples.

6.11 90 mm acid prewashed filters: The filters should be constructed of borosilicate glass fiber with no binder materials. The filters shall have an effective pore sized of 6 to 8 microns. <u>Pre-filtration of the extract is not an acceptable practice.</u>

6.12 Carboys, 10 to 20 Liters, for extraction fluids.

6.13 Compressed Nitrogen for use in pressurizing the TCLP/SPLP extractors.

6.14 Miscellaneous laboratory glassware such as beaker, flasks, and pipettes.

6.15 Sample bottles for extract storage.

6.16 Magnetic Stirrer.

6.17 Zero Headspace Extractor (ZHE): this device is used only when the waste is being tested for volatiles. The ZHE allows for liquid/solid separation, and effectively precludes headspace. The vessel allows for initial liquid/solid separation, extraction, and final filtration without opening the vessel. The vessel shall have an internal volume of 500-600 mL and be equipped to accommodate a 90-110 mm filter. The device contains VITON o-rings that should be replaced frequently. The piston within the ZHE should be able to be moved with approximately 15 psi. If the piston does not move with 15 psi then the extractor must be taken out of use and must not be used until repaired. Each extractor should be uniquely numbered.

6.18 Cleaning Procedure for Zero Headspace Extractor

- Wash with soap and hot tap water.
- Rinse with deionized water a minimum of 3 times.

6.19 45 mm filters: The filters should be constructed of borosilicate glass fiber with no binder materials. The filters shall have an effective pore size of 6 to 8 microns.

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6.20 Filter screens: 44 mm or 90 mm diameter.

6.21 Tygon Tubing

7.0 Reagents and Standards

7.1 The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

7.2 Deionized Water: Prepare by passing water through a mixed bed of cation and anion exchange resins or an equivalent source.

7.3 Hydrochloric Acid, 1 N: Dilute 83 mL concentrated HCl to 1000 mL volumetrically with deionized water. **Note: Add acid to water!** Shelf life: 1 year.

7.4 Nitric Acid, 1 N: Dilute 64 mL concentrated HNO_3 to 1000 mL volumetrically with deionized water. Note: **Add acid to water!** Shelf life: 1 year.

7.5 Acetic Acid, Glacial.

7.6 Sulfuric acid/Nitric acid 60/40 Mixture. Cautiously mix 60 g concentrated sulfuric acid with 40 g concentrated nitric acid.

7.7 Sodium Hydroxide, 10 N: Dissolve 400 g NaOH in 500 mL deionized water and dilute to 1000 mL with deionized water. Shelf life: 1 year.

7.8 TCLP Extraction Fluid #1: 114 mL glacial acetic acid diluted to 10 L with deionized water. Add 129 ml 10N NaOH, and dilute to 20 L with deionized water. When correctly prepared, the pH of this solution will be 4.93 ± 0.05 units. Measure and record pH of solution with each use.

7.9 SPLP Extraction Fluid #1: Add the 60/40 Sulfuric acid/Nitric acid mixture to deionized water until the pH is 4.20 ± 0.05. Note that this solution is unbuffered and exact pH may not be obtained. This solution is used for leaching soils from sites east of the Mississippi River and for wastes and wastewaters.

7.10 TCLP Extraction Fluid #2: Dilute 22.8 mL glacial acetic acid to 4 L with deionized water. When correctly prepared, the pH of this solution will be 2.88 ± 0.05 units. Measure and record pH of solution with each use.

7.11 SPLP Extraction Fluid #2: Add the 60/40 Sulfuric acid/Nitric acid mixture to deionized water until the pH is 5.00 ± 0.05. Note that this solution is unbuffered and exact pH may not be obtained. This solution is used for leaching soils from sites west of the Mississippi River.

7.12 TCLP Extraction Fluid #3: (as referenced in OAC 3745-30-03 and described in ASTM D 3987-85): Deionized water.

7.13 SPLP Extraction Fluid #3: Deionized water. This is used for cyanide determination and volatiles leachability.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

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Preservation Table

Matrix	Sample Container	Min. Sample Size	Preservation*	Reference
Water	Glass	5 x 1L amber wide mouth	None	40 CFR Part 136
Soil	Glass	1 L wide mouth	None	NA

*Preservative must not be added to the waste prior to extraction. All samples may be refrigerated unless refrigeration results in irreversible physical change to the waste.

Extracts shall be split and preserved in accordance with the individual analytical methods. Extracts must be processed through method extractions per the analytical procedures. Any spiking solutions must be added prior to preservation of the metals extracts.

Holding Times Table**

Parameter	From Field collection to TCLP/SPLP Extraction	From TCLP/SPLP Extraction to Method Preparation	From Method Preparation to Determinative Analysis.
Volatiles	14	NA	14
Semi-Volatiles	14	7	40
Mercury	28	NA	28
Metals, except Hg	180	NA	180

**Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

9.0 Quality Control

The following quality control samples are prepared:

Quality Controls	Frequency	Control Limit
ZHE Vessel Blank*	1 per 20 extractions in a vessel	< RL
Fluid Blank	1 per batch of fluid	< RL

* Each ZHE vessel is assigned a unique identification, such as A, B, C etc. For every 20 ZHE samples that a vessel extracts, a vessel blank must be extracted.

9.1 Matrix spikes are not generated by the leaching group, but rather by the prep or extraction group.

9.2 ZHE Leak Checks are performed prior to each use.

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- Pressurize to 50 psi; submerge the ZHE vessel in water and check for the presence of air bubbles around the fittings. If the ZHE does not hold pressure check all O-rings and fittings. If the leaks cannot be stopped the extractor must be removed from service.

9.3 Extraction Temperature is monitored for each batch with the use of minimum/maximum thermometer. The thermometer is reset prior to the beginning of each extraction batch. The minimum and maximum temperature for an extraction batch is recorded in the extraction log.

- The extraction temperature for both the bottle extractors and the ZHEs should be maintained at 23 ± 2°C.

9.4 Agitator Check is performed with every batch.

- The agitator should rotate end-over-end at a rate of 30 ± 2 rpm. If the agitator cannot rotate at that rate, it should be removed from service.
- The rotations per minute (rpm) are counted with the agitator loaded full for 3 minutes. The average number of rotations per minute is recorded in the extraction log.

10.0 Procedure

Preliminary Evaluations include: (1) determination of 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 requires particle size reduction; and (4) determination of which of the extraction fluids are to be used.

10.1 Percent Solids Determination:

10.1.1 If the waste will obviously yield no free liquid when subjected to filtration, proceed to Section 10.2. (Particle Size Determination). This determination can be made by simple observation.

10.1.2 If the sample is liquid or multiphasic, liquid/solid separation is required to determine the percent solids.

- Pre-weigh the filter and/or the container that will receive the filtrate.
- In a beaker, weigh out a 100-gram (minimum) aliquot of the waste. (Record the exact weight of the waste).
- To ease filtration, allow slurries to stand to permit the solid phase of the waste to settle. Wastes may be centrifuged prior to filtration.
- Assemble the filtration apparatus. Transfer the waste to the filtration apparatus, spreading the waste evenly over the filter.
- Gradually apply vacuum or pressure of 1-10 psi. If liquid ceases to pass through the filter for a 2-minute period, slowly increase the pressure in increments of 10 psi to a maximum of 50 psi. When liquid has ceased to flow through the filter at 50 psi for a 2-minute period, stop the filtration. The material in the filter holder is defined as the solid phase, and the filtrate is defined as the liquid phase. NOTE: Instantaneous application of high pressure can degrade the filter and may cause premature clogging.
- Determine the weight of the solid and liquid phases. Calculate the percent solids as shown in Section 11. If the % solids determined is equal to or greater than 0.5%, proceed to the Particle Size Evaluation Section. If the % solids are less than 0.5%, the filtrate is considered the extract for non-volatiles and is ready for analysis. For volatile analysis, the waste will need to be filtered using the ZHE as described in Section 10.5.7.

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10.1.3 Use of dry weight total solids to demonstrate that a sample has less than 0.5% solids is guided as follows:

- If the sample has a low solid content, 1-5%, and it is suspected that entrapped water or oil has contributed substantially to the total solids, then the filter may be air-dried and a dry weight total solid determined. If the dry weight total solids is <0.5%, then the solids do not need to be extracted.

10.1.4 If a homogenous aliquot is requested, but can not be obtained, a representative sample may be obtained by taking aliquots of each phase in a manner that maintains the original proportions. Example: if a sample consists of two phases (80% upper phase and 20% lower phase) *, pipette 80 mL of the upper phase and 20 mL of the lower phase for initial evaluation of the percent total solids. If the sample filters and then separates into two phases, the phases will need to be split and analyzed separately. The results of the analyses will need to be combined mathematically In order to do this; the original volume of each phase must be recorded. The client should be notified when this occurs.

*One method of determining the relative volume of the different phases:

- Pour the liquid phases into a graduated cylinder. Measure the volumes of the phases. Measure the density of the phases. Calculate the weight of each.
- Weigh the total amount solids.
- The recombination calculation is then done based on the weight ratio of the phases.

10.2 Particle Size Evaluation:

10.2.1 The solid portion of the waste must be smaller than 1 cm in its narrowest dimension. If the waste contains particles larger than 1 cm, it must be reduced by crushing, grinding or cutting until it can pass through a 9.5 mm (0.375 inch) standard sieve.

10.2.2 Size reduction is not required if the sample surface area is greater than or equal to 3.1cm2 per gram. This would be typical of many filamentous materials- such as paper, cloth etc. Actual measurement of surface area is not required, nor is it recommended.

10.2.3 Special precautions must be taken when doing particle size reduction on wastes that require volatile analysis. Samples must be handled as little as possible. Sieving should only be done when absolutely necessary. Particle size reduction on wastes that require volatile analysis should be done at 4° C if possible. Heat should not be generated in the particle size reduction procedure.

10.3 Determination of Extraction Fluid:

10.3.1 TCLP

10.3.1.1 There are three different fluids that can be used with this extraction procedure. These fluids are described in Section 7. Extraction fluids #1 and #2 are used most frequently. The client may request fluid #3 if the waste is being analyzed under OAC 3745-30-03. If the client does not request the water extraction (Fluid #3) extraction fluid #1 is used for volatiles. If the extraction is for non-volatiles (Bottle extractor) the sample pH must be determined to select the proper extraction fluid.

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10.3.1.2 If the solid content is greater than or equal to 0.5%, and if the non-volatile extraction is to be performed, determine the appropriate fluid to use for the extraction as follows:

- 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, and transfer 5.0 grams to a glass beaker. The small particle size may require additional grinding or crushing. It is important to take a representative sample for grinding and crushing.
- Add 96.5 mL reagent water and stir the sample on a magnetic stirrer for 5 minutes. Measure and record pH. If the pH is $\leq$ 5.0, use extraction fluid #1. Proceed to the non-volatile extraction.
- If the pH is > 5.0, add 3.5 mL 1N HCL, and stir briefly. Heat sample on hot plate producing a sample temperature of 50°C, which is maintained for 10 minutes.
- Let the solution cool to room temperature and immediately measure and record pH. If the pH is $\leq$ 5.0, use extraction fluid #1. If the pH is > 5.0, use extraction fluid #2. Proceed to the non-volatile extraction.

10.3.2 SPLP:

10.3.2.1 Use SPLP Fluid #1 for leaching soils from sites East of the Mississippi River and for wastes and wastewaters.

10.3.2.2 Use SPLP Fluid #2 for leaching soils from sites West of the Mississippi River.

10.3.2.3 Use SPLP Fluid #3 for cyanide determination and for leaching volatiles.

10.4 Non-volatile Extraction

Initially, a minimum sample size of 100 grams is required for the separation of the liquids from the solid, if liquid is present. Enough solids should be used for the extraction such that the volume of extract will be sufficient to support all of the analyses required.

10.4.1 If the waste will obviously yield no liquid when subjected to filtration, weigh out a subsample of waste (100 g minimum) and proceed to Section 10.4.3.

10.4.2 If the sample is liquid or multiphasic, liquid/solid separation is required.

- Pre-weigh the container that will receive the filtrate and/or the filter that will be used.
- Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. If evaluating the mobility of metals, make sure that acid washed filters are used.

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

- Weigh out a subsample of waste (100 gram minimum) and record the weight. If the waste contains <0.5% solids, the filtrate is defined as the TCLP/SPLP extract. Enough of the sample should be filtered so that the amount of filtrate will support the required analyses. If the waste contains >0.5% solids, use the % solids information obtained to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP/SPLP extract as well as to get a representative sample.

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For example: If the sample is 10% solids, after filtration of 100 g sample you would have 90 g filtered liquid and 10 g solid. 200 g (20 x 10 g) of extraction fluid would be added to the solid for extraction. This would yield approximately 290 mL final extract. If volume is insufficient, more sample must be filtered.

- Transfer the waste to the filtration apparatus, spreading the waste evenly over the filter. Gradually apply vacuum or pressure of 1-10 psi. If liquid ceases to pass through the filter for a 2-minute period, slowly increase the pressure in increments of 10 psi to a maximum of 50 psi. When liquid has ceased to flow through the filter at 50psi for a 2-minute period, stop the filtration.

NOTE: Instantaneous application high pressure can degrade the filter and may cause premature clogging. Additionally, some wastes such as oily wastes and paint wastes will contain material that appears to be liquid. Even after applying pressure filtration this material may not filter. If this is the case, the liquid material within the filtration device is defined as a solid. Do not replace the original filter under any circumstances. Use only one filter.

- The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid portion of the waste. Weigh the filtrate or alternatively, weigh the filter and calculate the percent total solids. The liquid phase may be either analyzed or stored at 4°C until time of analysis.
- If the waste contains >0.5% solids, ensure that the particle size is 1 cm or less and transfer solids to the extractor bottle.

10.4.3 Prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area of particle-size as described in Section 10.2.1. 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.

10.4.4 Determine the amount of extraction fluid to add to the extractor vessel as follows:

Weight of Extraction Fluid (in g) = 20 x Weight of Sample (in g) X Percent Solids

For example: Assume 100 g of 80% solids waste filtered

20 x 0.80 x 100g = 1600 g extraction fluid added to solid for extraction

10.4.5 Slowly add this amount of the appropriate extraction fluid to the extractor vessel. Secure in a rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Record the start date and time in the extraction log. Measure and record the rotation rate as detailed in Section 9.4. Re-set the min/max thermometer. The room temperature should be maintained at 23 ± 2°C.

NOTE: As agitation continues, pressure may build up in an extraction bottle. To relieve excess pressure, the extraction bottle may be opened up periodically and vented under a hood.

10.4.6 Following the 18-hour extraction, separate the material in the extractor bottle into solid and liquid phases by filtering through an acid-washed glass fiber filter. Record the stop date and time in the extraction logbook, and read the min/max thermometer and record in the extraction logbook.

10.4.7 Prepare the extract as follows:

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- If the material contained no initial liquid phase, the filtered liquid material is defined as the TCLP/SPLP extract.
- If the waste contained initial liquid, combine this liquid (if compatible) with the extract. This combined liquid is defined as the TCLP/SPLP extract.
- If the filtered extract is not compatible with the initial phase obtained prior to the extraction do not combine these liquids. Analyze these liquids separately, and combine the results mathematically as describe in the next section. The volume of extract produced and the volume of filtrate produced must be recorded in order to perform the calculation.

10.4.8 Following the collection of the TCLP/SPLP extract, the pH of the extract shall be recorded. Immediately split and preserve the extract for analysis. Metals must be acidified with nitric acid to a pH of <2. Take separate aliquots for the metals and organics spike sample. **Do not preserve the metals spike sample until after spiking appropriately.** All other aliquots must be stored at 4°C until analysis. The Metals Department is responsible for preserving the metals fraction upon completion of the bottle extraction and filtration. The metals spike is added as described in the Metals Preparation SOPs. If the sample preparation is not done immediately the extract should be spiked and preserved as described earlier in this section. The other non-volatile fractions do not require chemical preservation but should be stored at 4°C until analysis.

10.5 Volatile – Zero Headspace (ZHE) Extraction

10.5.1 Use the ZHE device to obtain the TCLP/SPLP extract for volatiles only. Extracts resulting from the ZHE shall not be used for any non-volatile analysis. The ZHE has a volume of approximately 500mL. The unit can thus accept a maximum of 25 grams of solid material. 25 grams of solid material is defined as the fraction of sample from which no additional liquid may be forced out by an applied pressure of 50 psi. Charge the sample only once and do not open the device until the final extract has been collected.

10.5.2 Determine the percent solids with a representative subsample as in Section 8.2. This step is not necessary if the solids content was already determined in the non-volatile extraction.

10.5.3 If the solids content is <0.5%, after fresh sample has been filtered through the ZHE unit and collected in a VOA vial, the solid phase may be discarded and the liquid phase is considered the extract. The sample is ready for analysis.

10.5.4 If the waste is > 0.5% and < 5% solids, weigh out a 500-gram subsample and record the weight. Calculate the amount of solid left in the ZHE filtration unit after initial filtration.

(500 x % solids) = amount of solid material that will be left in the ZHE

10.5.5 If the waste is greater than or equal to 5% solids and less than 100%, calculate the sample weight to be used by using the following equation:

$$\text{Weight to be used (in g)} = \frac{25g}{\%\ \text{Solids}}$$

For Example, assume 10% solids:

$$\text{Weight to be used (in g)} = \frac{25g}{0.10} = 250 \text{ grams}$$

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Weigh out the subsample to the calculated weight and record.

10.5.6 If the waste is 100% solid, weigh out a 25-gram subsample of the waste and record weight.

- Ensure that the solid portion of the waste has a particle size of 1 cm or less. If necessary, reduce particle size by crushing, grinding, or cutting solid portion of waste. Exposure of the waste to the atmosphere should be avoided to the extent possible.
- The sample and the size reduction equipment should be refrigerated to 4° C to reduce volatile loss. The use of sieving is not recommended. The use of an appropriately graduated ruler is an acceptable alternative.
- Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

10.5.7 Transfer the required amount of sample to the ZHE. Secure the filter and support screens to the ZHE body. A tight seal can be obtained by wetting the O-ring before fitting it into place. Tighten all fitting it into place. Tighten all fittings and place the device into a vertical position. 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 about 1-10 psi to force out all headspace out of the ZHE. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If the waste is 100 % solid, slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device.

10.5.8 The material remaining in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase. Note: Some oils and paints will not filter and should be treated as 100% solids.

10.5.9 The liquid phase collected in the VOA vial can now be stored at 4 $\pm$ 2°C under minimal headspace conditions until it can be combined with the extract from the solid phase.

10.5.10 Determine the weight of the extraction fluid to add to the ZHE as follows:

Weight of Extraction Fluid (in Grams) = 20 x Weight of Sample X Percent Solids
(The volume should be determined by <u>weight basis</u> not volume basis)

For example: Assume 250 g of 10% solids waste filtered
20 x 0.10 x 250g = 500 g extraction fluid added to solid for extraction

The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE vessel utilizing a dispensing pressure vessel. Extraction fluid #1 is used except when the client requests the water extraction fluid (Extraction Fluid 3) described in OAC 3645-30-03.

10.5.11 The dispensing pressure vessel is designed to automatically deliver the proper amount of extraction fluid when 25 g of solid material is contained in the ZHE unit. With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. Pressurize the vessel to a maximum of 50 psi. Release the pressure at the tank after pressurizing the vessel. The line must be pre-flushed with extraction fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (using the gas inlet/outlet valve), open

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the liquid inlet/outlet valve, and begin transferring extraction liquid into the ZHE until the appropriate amount of fluid has been introduced into the device.

10.5.12 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the 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. Pressurize the ZHE to 5-10 psi and slowly open the liquid inlet/outlet valve to bleed out any headspace. 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.

10.5.13 Check the ZHE vessel for leaks.

10.5.14 Place the ZHE in the rotary apparatus and rotate at 30 ± 2 rpm for 18 ± 2 hours. The room temperature should be maintained at 23 ± 2°C. Record the temperature of the room in the TCLP/SPLP/ZHE Exaction Logbook.

10.5.15 Following the extraction, check the pressure behind the ZHE piston by quickly opening the inlet/outlet valve and noting the escape of gas. If pressure has not been maintained (i.e. no gas released) the device is leaking. Replace the o-rings or fittings, as necessary, and repeat the extraction. If the pressure has been maintained, the material in the extractor is once again separated into its liquid and solid phase using the ZHE apparatus. The liquid phase should be collected in pre-preserved VOA vials with minimal headspace. The ZHE extractor inlet/outlet valve should be opened and the fluid should be drained slowly into the VOA vial with a minimum of air bubbles introduced. When the vial is completely filled to the top of the vial, cap the vial making sure that there are no air bubbles evident.

10.5.16 If the waste contained an initial liquid phase, this liquid shall be combined with the filtered extract. Composite the initial with the final extract. If the waste had an initial liquid phase all of the extract must be filtered, and composited into VOA vials. Compositing is required unless doing so would create multiple phases. In this case, analyze the samples separately, and determine the concentration mathematically.

10.5.17 If the waste contained no initial liquid, the filtered material is defined as the volatile TCLP extract. The volatile TCLP fraction does not require chemical preservation but should be stored at 4° C until analysis.

10.5.18 Please see the individual RCRA analytical SOPs for information concerning the analysis of the waste extracts.

11.0 Calculations / Data Reduction

11.1 Percent Solids in Preliminary Evaluations

$$\% \text{ Solids} = \frac{\text{Weight of solid}}{\text{Total Weight of Waste}} \times 100\%$$

11.2 Weight of Extraction Fluid

Weight of Extraction Fluid (in Grams) = 20 x Weight of Sample X Percent Solids

(The volume should be determined by weight basis not volume basis)

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11.3 If the individual phases are to be analyzed separately, determine the volume of the individual phases, conduct the appropriate analyses, and combine the results mathematically as follows:

$$\text{Final Analyte Concentration} = \frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$$

Where: V1 = Volume of the first phase (L)
C1 = Concentration of the contaminant of concern in the first phase (mg/L)
V2 = Volume of the second phase (L)
C2 = Concentration of the contaminant of concern in the second phase (mg/L)

12.0 Method Performance

12.1 Method Detection Limit Study - MDL studies are not performed for TCLP/SPLP matrix. The water MDL studies are used.

12.2 Training Requirements – Training requirements and documentation are described in the TestAmerica Dayton QA Manual (DT-QAM-001).

12.3 Demonstration of Capability for TCLP leaching is typically documented via copies of logbook pages from 4 batches and Department Manager approval describing method competency.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

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 Dayton's facility addendum.

14.1 The following waste streams are produced when this method is carried out.

- Acidic and/or alkaline sample waste generated by the analysis is neutralized and discharged to the sanitary sewer.
- Solid sample waste and used filter paper from sample filtration steps is disposed of in the general trash.

15.0 References / Cross-References

15.1 USEPA SW 846, "Method 1311: Toxicity Characteristic Leaching Procedure", Office of Solid Waste, Revision 0, July 1992.

SEE AMENDMENT AT FRONT OF DOCUMENT

15.2 American Society for Testing of Materials, "D 3987-85: Standard Test Method for Shake Extraction of Solid Waste with Water", 1985.

15.3 Ohio Administrative Code, "3745-30-03: Residual Waste Characterization", 1994.

15.4 USEPA Region 2 RCRA Outreach Program, "EPA-902-B-94-001: Technical Assistance Document for Complying with the TC rule and implementing the Toxicity Characteristic Leaching Procedure (TCLP)", May 1994.

15.5 TestAmerica Dayton QA Manual, DT-QAM-001.

15.6 TestAmerica Company Wide Environmental Health and Safety Manual, CW-E-M-001.

16.0 Method Modifications

Item	Method	Modification
5.5	SW-846 Method 1311	10N Sodium Hydroxide is used.

17.0 Attachments

Figure 1 TCLP/ZHE Extraction Log

Figure 2 SPLP Extraction Log

18.0 Revision History

18.1 Revision Dates

- 01/04/2011- Biennial review
- 12/24/2008 Original (replaces DT05-02.6)

18.2 Changes from last revision

Section	Change from	Change to	Reason
Copyright	2008 info	2010 info	Corrected for annual update
4.2	Added	If samples are multi-phasic, the client should be consulted to determine if separate analyses are requested on each layer.	Define procedure
4.3	Added	Note that for Oily wastes, a TCLP leach may not be required:	Clarify that this memo is for Oily wastes
8.0 preservation table	Cool <6.0°C but not frozen	None	Corporate QA interpretation is that if the refrigeration is optional based on sample reaction, then it can not be required.
8.0 preservation table	All samples must be	All samples may be	Corporate QA interpretation is that if the refrigeration is optional based on sample reaction, then it can not be required.

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Section	Change from	Change to	Reason
10.1.1	Added	This determination can be made by simple observation.	Clarify procedure
10.1.4	Added	* One method of determining the relative volume of the different phases: • Pour the liquid phases into a graduated cylinder. Measure the volumes of the phases. Measure the density of the phases. Calculate the weight of each. • Weigh the total amount solids. • The recombination calculation is then done based on the weight ratio of the phases.	Clarify procedure
10.2.2	Added	Size reduction is not required if the sample surface area is greater than or equal to 3.1cm2 per gram. This would be typical of many filamentous materials- such as paper, cloth etc. Actual measurement of surface area is not required, nor is it recommended.	Clarify requirements
12.3	Added	Demonstrations of Capability for TCLP leaching are typically documented via copies of logbook pages from 4 batches and Department Manager approval describing method competency.	Clarify procedure

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SEE AMENDMENT AT FRONT OF DOCUMENT

Figure 1 EXAMPLE TCLP Extraction Log

Analyst: _____ Date: _____

Min/Max Room Temperature (in °C): _____
Note: Room temperature must be 21 - 25°C

Extraction Fluid 1 Lot #: _____ pH: _____
Note: pH must be 4.88-4.98

Rotation Rate: _____
Note: Rotator rate must be 28-32 rpm

Extraction Fluid 2 Lot #: _____ pH: _____
Note: pH must be 2.83-2.93

Rotation Start Date/Time: _____

Rotation Stop Date/Time: _____

Check One: TCLP_____ ZHE_____

Sample ID				
ZHE Identification				
ZHE Leak Check				
1. Determination of Percent Solids – (Check a or b)				
a) Sample is 100% Solid (check & go to step 3).				
b) Sample is part liquid or multi-phased (check & go to step 2).				
2. Pressure Filtration using an acid washed glass fiber filter				
Weight of Sample (A)				
Apply vacuum in increments of 10 psi up to 50 psi or until filtering stops for 2 minutes.				
Weight of Sample after filtration (B)				
% Solids = (B/A) X 100%				
If %Solids >0.5%, Record volume of filtrate (in mL), store Filtrate for combination with TCLP leachate. Go to step 3.				
If %Solids < 0.5%, the filtrate is the TCLP leachate (check here and go to step 7).				
3. Determination if Solid Phase needs Particle Size Reduction				
If solid phase would pass through a 9.5 mm sieve, check here and go to step 4.				
If not, prepare solid portion by crushing, cutting, or grinding. For ZHE, used chilled implements.				

SEE AMENDMENT AT FRONT OF DOCUMENT

Sample ID				
Check here and go to step 4.				
4. Extraction Fluid Determination				
Fluid 3: If directed by client, use Fluid 3 (DI water) and check here.				
Sample ID				
ZHE – If not directed by client to use Fluid 3, use Fluid 1 and check here.				
TCLP Fluid Determination				
Weight of sample (5 gms)				
Add 96.5 mLs water.				
Stir 5 minutes, record pH If Initial pH is ≤5, use Extraction Fluid 1				
If Initial pH is >5, add 3.5 mls of 1N HCl, heat to 50°C and hold at 50°C for ten minutes.				
Let cool to room temperature and record Final pH. If Final pH ≤ 5 use Fluid 1. If Final pH > 5 use Fluid 2.				
5. Extraction Procedure				
Weight of Sample				
Add 20 times the amount of extraction fluid to the sample. Record the weight of the extraction fluid.				
6. TCLP/ZHE Rotation				
Reset Min/Max Thermometer				
Record Start Date/Time, Rotation Rate above.				
Record Stop Date/Time and Min/Max Room Temperature above.				
Filter leachate using an acid washed glass fiber filter.				
Record pH of TCLP leachate.				
7. For Multi-phase samples ONLY.				
Volume (mL) of Filtrate from Step 2.				
Volume (mL) of Leachate.				

SEE AMENDMENT AT FRONT OF DOCUMENT

Sample ID				
If filtrate and leachate are compatible, combine them and check here.				
Record Combined Volume (mL).				
Record pH of Combined Volume.				
If filtrate and leachate are not compatible, check here and extract them separately.				

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SEE AMENDMENT AT FRONT OF DOCUMENT

Figure 2 EXAMPLE SPLP Extraction Log

Analyst: _____ Date: _____

Min/Max Room Temperature (in °C): _____
Note: Room temperature must be 21 - 25°C

Extraction Fluid 1 Lot #: _____ pH: _____
Note: pH must be 4.15-4.25

Rotation Rate: _____
Note: Rotator rate must be 28-32 rpm

Extraction Fluid 2 Lot #: _____ pH: _____
Note: pH must be 4.95-5.05

Rotation Start Date/Time: _____

Rotation Stop Date/Time: _____

Check One: SPLP_____ ZHE_____

Sample ID				
ZHE Identification				
ZHE Leak Check				
1. Determination of Percent Solids – (Check a or b)				
a) Sample is 100% Solid (check & go to step 3).				
b) Sample is part liquid or multi-phased (check & go to step 2).				
2. Pressure Filtration using an acid washed glass fiber filter				
Weight of Sample (A)				
Apply vacuum in increments of 10 psi up to 50 psi or until filtering stops for 2 minutes.				
Weight of Sample after filtration (B)				
% Solids = (B/A) X 100%				
If %Solids >0.5%, Record volume of filtrate (in mL), store Filtrate for combination with TCLP leachate. Go to step 3.				
If %Solids < 0.5%, the filtrate is the TCLP leachate (check here and go to step 7).				
3. Determination if Solid Phase needs Particle Size Reduction				
If solid phase would pass through a 9.5 mm sieve, check here and go to step 4.				
If not, prepare solid portion by crushing, cutting, or grinding. For ZHE, used chilled implements.				

SEE AMENDMENT ATTACHED FRONT OF DOCUMENT

Sample ID				
Check here and go to step 4.				
4. Extraction Fluid Used				
Sample ID				
ZHE –Use Fluid 3 (DI water)and check here.				
If for cyanide determination - Use Fluid 3 (DI water) and check here				
For soils originating west of the Mississippi use SPLP Fluid 2 and check here				
For wastes, wastewaters and soils originating east of the Mississippi use SPLP Fluid 1 and check here				
5. Extraction Procedure				
Weight of Sample				
Add 20 times the amount of extraction fluid to the sample. Record the weight of the extraction fluid.				
6. SPLP/ZHE Rotation				
Reset Min/Max Thermometer				
Record Start Date/Time, Rotation Rate above.				
Record Stop Date/Time and Min/Max Room Temperature above.				
Filter leachate using an acid washed glass fiber filter.				
Record pH of SPLP leachate.				
7. For Multi-phase samples ONLY.				
Volume (mL) of Filtrate from Step 2.				
Volume (mL) of Leachate.				
If filtrate and leachate are compatible, combine them and check here.				
Record Combined Volume (mL).				
Record pH of Combined Volume.				
If filtrate and leachate are not compatible, check here and extract them separately.				

Title: SW-846 8260A/B – Volatile Organic Compounds by GC/MS

USEPA SW-846 8260A, 8260B and 8000B

Approvals (Signature/Date):

3/30/2011		3/30/2011	
Josh McKinney	Date	Jason Lykins	Date
Department Manager	EH&S	Officer	
3/28/2011		3/31/2011	
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1.0 Scope and Application

1.1 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra.

1.2 For the purposes of this procedure, 8260A and 8260B are distinguished by the sampling technique used to collect the samples. All waters may be reported by 8260B. If soils are collected in a manner consistent with 5035A, then they may be reported by 8260B, otherwise they are reported as 8260A.

1.3 Method 8260 is used to determine volatile organic compounds in a variety of matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils and sediments. See Table 1 for compounds amenable by Method 8260.

- Additional compounds may be analyzed using this procedure, provided all appropriate quality control measures are evaluated and found acceptable. For OVAP, only compounds listed in the method may be reported using this procedure (with the exception of n-Hexane which requires specific certification)

1.4 There are various techniques by which these compounds may be introduced into the GC/MS system. Purge-and-trap, by Method 5030 (aqueous and solid samples) and 5035A (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. Method 5000 provides more general information on the selection of the appropriate introduction method.

1.5 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200 ^{o}C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of the poor purging efficiency. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers and sulfides.

1.6 The Method Reporting Limit (MRL) of Method 8260 for an individual compound is somewhat instrument dependent. Limits are approximately 5 µg/Kg (wet weight) for soil/sediment samples, 0.5 mg/Kg (wet weight) for wastes, and 1 µg/L for ground water. See Table 1 for Example soil and water reporting limits. MRLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used.

1.7 Method 8260 is based on a purge-and-trap, gas chromatography/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and GC/MS and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.8 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated in DT-QAM-001, Quality Assurance Manual. **OVAP does not allow modifications to the SOP.**

2.0 Summary of Method

2.1 The volatile compounds are introduced into the GC by the purge-and-trap method. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and back flushed with helium (or nitrogen) to desorb trapped sample components. The analytes are desorbed directly to a narrow

bore or wide bore capillary column for analysis. The column is temperature programmed to separate the analytes that are then detected with a MS interfaced to the GC. Wide bore capillary columns require a jet separator, whereas narrow bore capillary columns can be directly interfaced to the ion source.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in solvent to dissolve the volatile organic constituents. A portion of the solution is combined with organic-free reagent water in the purge chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 Analytes eluted from the capillary column are introduced into the MS via a jet separator or direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard with a five-point (minimum) calibration.

2.4 The method includes specific calibration and quality control steps that replace the general requirements in Method 8000.

3.0 Definitions

3.1 BTEX – acronym for the combination of Benzene, Toluene, Ethylbenzene, and Xylenes.

3.2 GC – Gas chromatograph

3.3 GC/MS – Gas Chromatograph Mass Spectrometer

3.4 VOC – volatile organic compound

3.5 EICP—Extracted Ion Current Profile, a plot of ion abu ndances versus time or scan number.

3.6 CCV – Continuing Calibration Verification.

3.7 SPCC – System performance check compounds.

3.8 CCC – Calibration Check Compounds

3.9 BFB – 4-Bromofluorobenzene, used as a surrogate and as a tune check.

3.10 IS – Internal Standard

3.11 MRL- Method Reporting Limit

3.12 Please see the Glossary in the Qualit y Assurance Manual, DT-QAM-0 01 for additional definitions.

4.0 Interferences

4.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks corrective action to remove the interfering substance must occur before sample analysis. Subtracting blank values from sample results is not permitted. If reporting values not corrected for blanks result in what the laboratory feels is a false positive for a sample, this should be fully explained in text accompanying the uncorrected data.

4.2 Interfering carryover contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. Repeat analysis of samples

that immediately follow a very high sample may be necessary. In extreme conditions, it may be necessary to rinse the purge-and-trap device and/or bake out the system for extended periods of time prior to sample analysis.

4.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random backround levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during organic extraction procedures can contribute to sample contamination.

4.4 Use of a sensitive MS to achieve lower detection levels will increase the potential to detect laboratory contaminants as interferences.

4.5 Septa bleed may occur with the heated purging of soils. Care must be taken to ensure that 40 mL vials selected for soil analysis contain low bleed septa. It is common to see a detection for o-Xylene with the wrong septa.

4.6 Crossover contamination from the environment and other samples is common with volatile samples. Care must be taken to ensure sample contamination does not occur. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination. Storage blanks from each refrigerator are monitored every 14 days for possible contamination.

4.7 If recovery failures occur, possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, active sites/leaks in the column or purge and trap system.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), 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

5.1.1 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.2 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.1.3 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

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 standards section. Employees must review the informa tion in the MSDS for e ach 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
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Agilent Technologies (formerly Hewlett Packard) 5890 or 6890 Gas Chromatograph with a 5970, 5972 or 5973 Mass Spectrometer. The system should be equipped with a glass jet separator if the capillary column cannot be directly coupled to the source (as is the case with the 6890/5973 using a split/splitless injection port).

6.2 Data system – A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. A copy of the EPA/NIST or Wiley Mass Spectral Library must also be available.

6.3 Varian Archon autosampler and a Tekmar 3000 / 3100 or EnCon purge-and-trap device to introduce the sample to the GC.

6.4 5-mL Sparger glassware with no side arms for the Tekmar 3000/3100.

6.5 DB-624 column. 75 m x 0.530 mm x 3.0 micron, J & W Scientific.

6.6 DB-624 column. 25 m x 0.20 mm x 1.12 micron, J & W Scientific.

6.7 Rx-624 column. 20 m x 0.18 mm x 1.0 micron, Restek.

6.8 Supelco Type K Trap (Vocarb 3000) for Tekmar 3000. Other appropriate traps may be substituted, but Purge-and-Trap operating conditions may need to be adjusted for trap changes. Prior to use, this trap should be conditioned at least one hour at normal instrument bake-out temperature with a helium (or nitrogen) backflush. Overnight conditioning is recommended.

6.9 Microsyringes, various sizes, for standard preparation and sample injection. 5-mL, 10-mL and 25-mL Luer lock syringes for sample /standard preparation.

6.10 Disposable plastic syringes, various sizes, for standard preparation and sample dilution.

6.11 Volumetric flasks, Class A, for standard preparation and sample dilution.

6.12 Calibrated VOA vials, for standard preparation and sample dilution.

6.13 Analytical balance, capable of accuracy to 0.0001 g.

6.14 40-ml VOA vials with low bleed septa.

6.15 EnCore™ Soil samplers and Extraction tools. EnNovative Technologies, Inc. or equivalent.

6.16 5- and 10-ml amber vials equipped with Mininert caps.

6.17 Disposable magnetic stir bars.

6.18 Wooden tongue depressors.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

7.1 Organic-free reagent water.

7.2 Methanol, purge-and-trap grade.

7.3 Bromofluorobenzene, Acros.

7.4 BFB Tune Check Standard (25 ng/µL) – Prepare a 2.5-mg/ mL standard by weighing 25 mg into a 10 mL volumetric containing some purge-and-trap methanol. Bring to volume with methanol. Dilute 1 mL of the 25 mg/10mL BFB standard to 100 mL with methanol in a 100 mL volumetric to give a 2.5mg/100 mL or 25 ng/µL. Transfer to 40 mL VOA vial for storage or a 2 mL autosampler vial. Other amounts of BFB may be used, but the amount injected onto column must be less than or equal to 50 ng.

7.5 8260 Primary Calibration Standards (See Table 2).

7.6 8260 Calibration Standards. Prepare a calibration curve as indicated in Tables 6a or 6b.

7.6.1 Calibration curves, ICVs and CCVs are matrix matched to the samples. If running soils, each standard contains 5g of sand.

7.6.2 Standards are prepared in volumetric flasks, or calibrated vials. Adjust amount of standard used accordingly.

7.6.3 To prepare a calibration standard, add an appropriate volume of a primary dilution standard containing all analytes of concern to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the methanol-based primary dilution standard solution into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable in a volumetric flask and must be discarded after a few minutes unless transferred to a sample bottle and sealed immediately.

- It is acceptable to prepare separate calibration curves for additional analytes- for example, Tetrahydrofuran is not part of the typical daily calibration. If analysis is requested, a separate calibration is analyzed.

7.6.4 Standards for aqueous calibrations should be transferred immediately to a 40 mL VOA vial with no headspace.

7.6.5 Standards for non-aqueous heated purge calibrations should be transferred immediately to a 5 mL or 10 mL Luer-lock syringe with no headspace. 5 mL is transferred to a 40 mL VOA vial and sealed immediately. 5035A low level soil calibration standards are added to vials containing 1g of sodium bisulfate when the corresponding samples contain sodium bisulfate. It is very important to ensure the vial is sealed properly because the vial will be the purge vessel and any leaks will result in loss of volatile compounds.

7.6.6 Calibration standards must be made fresh daily.

7.6.7 Surrogate and internal standard are added automatically by the autosampler and do not need to be added to the standards.

- Manual addition of the surrogates and internal standards is acceptable, but manual or automatic- the procedure must be the same for calibration and other QC as for the samples.

7.7 8260 ICV/LCS Stock Standard (See Table 3).

7.8 8260 ICV (20 µg/L). Prepare by injecting 5 µL of the 8260 ICV Primary Dilution Standard into a 50 mL volumetric flask containing organic-free reagent water. Mix as described above and transfer to 40 mL VOA vials for aqueous analysis. Transfer 5 mL to a 40 mL VOA vial and seal immediately for low-level soil calibrations. 5035A low level soil ICV should be added to a vial containing 1g of sodium bisulfate or 5g clean sand- depending on how the calibration was prepared. Prepared ICV is viable for no longer than 24 hours. An ICV must be analyzed with all initial calibrations to verify the calibration. The ICV may be prepared at other concentrations within the calibrated range.

7.9 8260 LCS (20 µg/L). Add 5 µL of the 8260 ICV (LCS) Mother to 50 mL of organic-free reagent water in a 50 mL volumetric flask. Mix as described above and transfer to 40 mL VOA vials for aqueous analysis. Transfer 5 mL to a 40 mL VOA vial and seal immediately for low-level soil calibrations. 5035A low level soil LCS should be added to a vial containing 1 g of sodium bisulfate or 5g of soil, depending on the sample preservation. Prepared LCS is viable for no longer than 24 hours. The LCS may be prepared at other concentrations within the calibrated range.

7.10 8260 CCV (50 µg/L). and 8260 LCS (20 µg/L). Prepare as described above for 50 ppb calibration standard. The CCV may be prepared at other concentrations within the calibrated range.

7.11 8260 Primary Surrogate Spike Solution (2500 µg/mL). Restek 30240 or equivalent.

7.12 8260 Primary Internal Standard Spike Solution (2500 µg/mL) Restek 30241 or equivalent.

7.13 8260 SIS (Surrogate/Internal Standard) Working Spike Solution (250 µg/mL). Add 1 mL of the 8260 Primary Surrogate Spike Solution and 1 mL of the 8260 Primary Internal Standard Spike Solution to a 10 mL volumetric containing purge-and-trap methanol and bring to volume with purge-and-trap methanol. Transfer to the Archon Spike Reservoir or a 20 mL VOA vial for storage.

7.14 8260 Medium Level LCS/MS/MSD Spike Solution (2000 µg/L). Restek 502.2 CAL2000 Mega-Mix (Cat. # 30431) or equivalent.

7.15 Sodium bisulfate.

7.16 Dow Corning Anti-foam C.

7.17 DPD Powder for determination of free chlorine.

7.18 Standards should be stored with minimal headspace and protected from light at –10°C or less as recommended by the standard manufacturer. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

7.19 Stock standards and calibration standards cannot be kept for more than six months. Standards for the permanent gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if the percent drift exceeds 20%. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should be monitored closely. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

7.20 Volatile standards must be stored in separate refrigerators from semi-volatile standards.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests.

OVAP and most other environmental samples require compliance with the information detailed in the analytical methods.

Listed below are the holding times and the references that include preservation requirements.

8.1 Separate aliquots, in 2-4oz jars minimum, of the samples should be collected if % solid determination is required.

8.2 Preservation Table:

Matrix/ collection technique *	Prep Method	Sample Container preferred *	Preservation	Storage	Holding time from collection to analysis	Analytical Method
Water; no residual chlorine present	5030B	3-40mL vials with Teflon-lined septum	1:1 HCl to pH <2	<6.0°C but not frozen	14 days (7 days if not preserved)	Report as 8260B
Water; residual chlorine present	5030B	3-40mL vials with Teflon-lined septum	25mg ascorbic acid or 3 mg sodium thiosulfate per 40mL † 1:1 HCl to pH <2	<6.0°C but not frozen	14 days (7 days if not preserved)	Report as 8260B
Soil; collect as grab	5030B/ 5035A	2-4oz jars with Teflon-lined septum	None	<6.0°C, but not frozen	14 days	Report as 8260A if low/medium level May report as 8260B if high level

Soil; collect with coring device May extrude/ preserve in field or at lab	5035A	3*5g Terracores (or similar device) and 1*4oz jar for % Moisture	5mL Methanol 5mL Water, then frozen to between -7 and -20°C None 5mL Water with 1g NaHSO4	<6.0°C, but not frozen -7 to -20°C -7 to -20°C <6.0°C, but not frozen	48 hrs, extended to 14 days if chemically preserved or frozen within 48 hrs from sampling.	Report as 8260B

† Caution: never add acid preservative directly to a de-chlorinating agent prior to sample collection.

8.3 Preparation of previously frozen samples:

8.3.1 If the corers have been frozen first extrude 5g samples into three separate tared VOA vials containing magnetic stirring bars, obtain the weight of soil added to the vials and record. If the samples were extruded before freezing obtain the weight of soil added to the vials and proceed to the next step.

8.3.2 Add 5 mL water to two of the vials. The water should contain 1g $NaHSO_4$ if chemical preservation is to be used. These vials are to be used for low level analysis.

8.3.3 Add 5 mL methanol to the third vial. This vial is for medium level analysis.

8.4 *For concrete and other unusual matrices, the samples may be collected in plastic bottles, plastic bags or other containers.

9.0 Quality Control

9.1 Preparation QC

Quality Controls	Frequency	Comments
Method Blank (MB)	1 per preparation batch[1]	For soils, use sand or other clean solid matrix
Laboratory Control Sample (LCS)	1 per preparation batch[1]	For soils, use sand or other clean solid matrix
Matrix Spike/Matrix Spike Duplicate (MS/MSD)[2]	1 per preparation batch[1]	If there is insufficient sample for an MS/MSD, note this on the bench-sheet, along with the reason
Surrogates	Each standard and sample	

[1]Preparation batch is limited to 20 samples

[2]The sample selection for MS/MSD is random, unless specifically requested by a client.

9.2 Analytical QC

Quality Controls	Frequency	Comments
Tune check (BFB)	1 per 12 hr clock	May be injected or purged. Initiates the 12 hr clock.
Calibration Verification Standard	1 per 12 hr clock	New Initial Calibration must be performed if CCV fails and corrective action does not result in an acceptable CCV
Initial Calibration	As needed	Minimum of 5 calibration points
Internal Standards	Each standard and sample	

9.3 **Method Blank -** A Method Blank must be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants.

9.3.1 One purge-and-trap Method Blank must be analyzed with each group of up to 20 samples.

9.3.2 When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the Method Blank associated with those samples (e.g., extracted with the samples) must be analyzed on at least one of those instruments.

9.3.3 Acceptance criteria is <MRL. If the Method Blank shows a detection above the required Method Reporting Limit, it must be reanalyzed. If this fails to correct the problem, all associated samples with concentrations above the Method Reporting Limit, for the detected analyte, must be re-extracted.

9.3.4 If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag detections for the failing analyte in the affected samples, LCS, MS/MSD with a “B”. For OVAP, provide an explanation in the QC narrative.

- If the associated samples are non-detect, then reanalysis of the Method Blank is not required and re-extraction of samples is not required.
- If the concentration found in the samples is >10X the concentration found in the Method Blank, reanalysis is not required, but data must be flagged. **This exception is not allowed by OVAP.**

9.4 **Laboratory Control Sample -** A LCS is analyzed in each 12-hour shift during which samples are analyzed. A mid-point standard (typically 20 µg/L for water or 20 µg/Kg for soils) is analyzed following the CCV. An LCS is also extracted with each Medium Level extraction. Other spike concentrations may be used. Any samples analyzed in a 12-hour batch with a failed LCS must be reanalyzed.

9.4.1 The LCS may be spiked with and/or evaluated for a limited list of target analytes, provided this is acceptable to the regulatory program for which samples are being analyzed.

9.4.2 If the LCS fails to meet criteria, then the extraction batch is considered out-of-control for the compounds that failed for all associated samples, and re-extraction/re-analysis for those compounds must be performed before results are reported

9.4.3 If there is insufficient sample or if re-extraction will result in missed hold times, re-

extraction of samples is not required. Flag detections for the failing analyte in the affected samples, LCS and Method Blanks, do not flag the MS/ MSD. For OVAP, provide an explanation in the QC narrative.

9.4.4 If the LCS recovery is high and the associated samples are <MRL, reanalysis is not required

9.4.5 This standard may be used as the CCV as long as it meets all CCV criteria for all target compounds in that run batch.

9.5 **Surrogates** –All samples and standards are spiked with four surrogates.

9.5.1 Only those surrogates associated with the analytes of interest need to be spiked and/or evaluated.

9.5.2 Established limits are maintained in the LIMS.

9.5.3 Any sample, including batch QC, with surrogates outside the control limits requires evaluation by the laboratory. Once the problem has been identified and addressed, corrective action may include the reanalysis of samples, or the extraction and analysis of new sample aliquots.

9.5.4 If the samples are for OVAP Program, then any sample extract, including Method Blank and or/LCS, with a surrogate outside the acceptance limits must be reanalyzed and/or re-extracted if a matrix effect cannot be demonstrated.

- If the individual sample surrogate recoveries are high, and the associated analytes are non-detect, then reanalysis and/or re-extraction is not necessary.
- If the Method Blank or LCS has high surrogate recovery, and the samples are non-detect for the associated analytes, then reanalysis of the batch is not necessary.
- If there is an obvious matrix effect as evidenced by chromatography, sample foaming, or other physical matrix issue, re-extraction is not required. Flag surrogate recovery in the individually affected samples, MS/MSD. For OVAP, provide an explanation in the QC narrative.
- If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag surrogate recovery in the individually affected samples, Method Blank, LCS, MS/MSD. For OVAP, provide an explanation in the QC narrative.

9.6 **MS/MSD** – One sample in each 12-hour shift or one sample in 20 is prepared in triplicate and two replicates are spiked with the LCS standard described above at 20 µg/L (or 20 µg/Kg). These replicates are known as the matrix spike (MS) and matrix spike duplicate (MSD).

9.6.1 The MS/MSD may be evaluated for a limited list of target analytes, provided this is acceptable to the regulatory program for which samples are being analyzed.

9.6.2 The MS/MSD acceptance criteria is maintained in LIMS. See Section 11 for percent recovery and RPD calculations.

9.6.3 If the MS/MSD is outside of acceptance limits, flag the affected analyte in the parent sample, MS & MSD.

9.6.4 MS/MSD is not used for batch control.

9.6.5 If insufficient sample has been provided for a MS/MSD then make a note in the appropriate raw data or logbook.

9.7 **BFB Tune Check**. Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 using a 5-50 ng injection or purging of 4-bromofluorobenzene (BFB). Inject no more than 2µL onto the GC column for direct injection or add no more than 16.8µL to

42mL of organic-free reagent water for purge-and-trap introduction of the BFB tune check. Analyses must not begin until these criteria are met. All subsequent injections must follow the same MS conditions. An accelerated GC temperature program for BFB (See Tables 9a & 9b) is often used. The injection of the BFB initiates the 12-hour batch or work shift. All samples analyzed must be injected within 12 hours of the BFB injection.

9.8 Alternatively, other documented tuning criteria may be used (e.g. CLP, Method 524 or manufacturer's instructions) provided the method performance is not adversely affected. All subsequent standards, samples, MS/MSDs, LCSs, and Method Blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

9.8.1 The mass spectrum of BFB may be acquired in the following manner. Tune evaluations usually utilize the "Autofind" function and are set up to look at the apex +/- 1 scan and average the three scans. Background correction is required prior to the start of the peak but no more than 20 scans before. <u>Background correction must not include any part of the target peak.</u>

9.8.2 Other Options or if Autofind Fails

- "Autofind" is not an option for all versions of software, or sometimes the instrument does not always correctly identify the apex when the peak is not perfectly shaped. In this case, manually identify and average the apex peak +/- 1 scan and background correct as in 9.8.1above.
- Or the scan across the peak at one half peak height may be averaged and background corrected.
- Changes such as adjustments to the repeller and ion focus lenses, adjusting the EM Voltage, etc. may be made prior to tune verification as long as <u>all</u> of the subsequent injections in the 12 hour tune cycle are analyzed under the same MS tune settings and it is documented in the run sequence log and/or maintenance log that an adjustment was made. Excessive adjusting (more than 2 tries) without clear documentation is not allowed. Necessary maintenance is performed and documented in instrument log.
- A single scan at the Apex (only) may also be used for the evaluation of the tune, background correction is still required.
- If source cleaning or other maintenance is performed then follow steps for tune evaluation above. The maintenance must be documented in the maintenance log and should be noted in the sequence run log. Note: If significant maintenance is performed, see methods 8000B or 8000C, then the instrument may require recalibration prior to proceeding. Tune evaluation printouts must include the chromatogram and spectra as well as the Tune evaluation information.

9.8.3 Since the limits are expressed in whole percentages, the results may be rounded to whole percentage before comparing to criteria when assessing the tune verification against the tune requirements. However, the comparison to the criteria is usually done automatically by the software and if the printout says "Fail" then there would have to be documentation of the hand calculation on the raw data and comparison to the criteria if the lab intends to still accept the tune.

9.8.4 The instrument tune parameters are contained in a file that is referenced by the analytical method. To avoid the chance of error, it is recommended that the tune file be overwritten rather than renamed when an instrument tune is performed, so that editing the reference in the analytical method is not necessary.

9.8.5 All MS tune settings must remain constant between running the tune check and all other samples. It is recommended that a separate tune method not be used,

however a separate method may be used as long as the MS conditions between the methods are the same so any changes that are made to the Mass Spec of Tune specifications in the analysis method are also made to the tune method.

9.8.6 Any sample analyzed following a BFB that failed the above criteria must be re-analyzed. If no sample is available for re-analysis, data should be flagged and the client notified of the deviation.

9.8.7 The laboratory must not subtract results of the Method Blank from any associated samples. Such "blank subtraction" is inappropriate. If the Method Blank results do not meet the acceptance criteria and reanalysis is not possible, then the data user should be provided with the sample results, the Method Blank results, and a discussion of the corrective actions undertaken by the laboratory.

9.8.8 Method Blanks may be used to check contamination by carryover from a high-concentration sample into subsequent samples. If the analytes in the high-concentration sample are not present in the subsequent analysis, then lack of carryover has been demonstrated.

9.9 **Internal Standards** –All samples and standards are spiked with three internal standards. Only those internal standards associated with the target analytes need to be evaluated.

9.9.1 Sample internal standard responses acceptance criteria is –50% to +100% of the response in the CCV for that 12 hour shift. Samples with failing internal standards must be evaluated to determine if re-analysis and/or dilution must be performed to correct the deviations.

9.9.2 For OVAP, samples must not be reported with failing internal standards. If there is potential for the direct analysis of the sample to cause harm to the analytical system, such as when a sample is foamy, or suspected to contain high levels of analyte or non-target contamination, then initial analysis of the sample may be performed at a dilution.

9.9.3 If a matrix effect is determined to impact the internal standards, the sample must be diluted or processed in another manner to bring the internal standard recoveries into limits.

9.9.4 Matrix interference may be apparent through chromatographic evidence or sample color, foaming or other physical characteristic.

9.9.5 Excessive dilution to correct recoveries at the expense of removing target analytes is not acceptable.

9.9.6 If there are not obvious interferences, one sample from each affected project is reprocessed and reanalyzed to confirm a possible matrix effect. Reanalysis is performed at the original dilution (or undiluted), unless the extract is dark or thick, or otherwise expected to cause problems with the analytical system. If the recoveries confirm or there is obvious interference, results are reported from the original analysis and a qualifier is added. If the internal standard recoveries from the reprocessed sample fulfill criteria, all affected samples are reprocessed and results from the re-analyses are reported. The goal being to report samples with passing internal standards from the least diluted run.

9.10 **Calibration range exceedence**. If any response exceeds the upper limit of the calibration, dilution of the sample is required to achieve a response that is within the calibration range. Low-level soil samples may require a methanol extraction (medium level) to achieve a response in the calibration range.

9.10.1 If any response exceeds the upper limit of the calibration range, dilution of the sample is required to achieve a response that is within the calibration range.

9.10.2 On rare occasions, a sample result that is slightly above calibration will result in a

value that is slightly below calibration when analyzed at a methanol extraction. If this can not be corrected by running less initial sample weight (no less the 1g) or through other means, then it is appropriate to report both results with appropriate flags and/or a narrative. NOTE: Data qualified in this manner may not be usable for OVAP.

9.10.3 **Carryover**. Any detection of a compound following a sample with a high-concentration detection for the same compound should be considered suspect of system carryover. Reanalysis is required to demonstrate carryover. The system should be considered contaminated until demonstrated otherwise via analysis of clean blanks or samples that show no contamination.

9.11 For Ohio VAP: The laboratory must implement corrective action procedures to resolve the deviation and limit qualification of the final results. The laboratory is not permitted to deviate from its VAP approved SOP if it intends to attest under affidavit that the "results" are VAP certified. When all corrective actions listed in the SOP have been exhausted, it may be necessary to use technical judgment in which case the decision process and rationale will be presented in the final report and/or affidavit **and the data will be noted as 'not VAP certified' on the affidavit.**

10.0 Procedure

10.1 Instrument Operating Conditions.

10.1.1 Recommended Purge and Trap Conditions. See Table 8 for the recommended purge-and-trap conditions. Install a Vocarb 3000 trap and condition for at least one hour at 280 ^{o}C. Overnight conditioning is recommended. The moisture control system and trap pressure valve are bypassed on the concentrators.

10.1.2 Recommended GC/MS Operating Conditions. See Tables 9a & 9b for the recommended GC/MS operating conditions. The two tables distinguish between systems operating with a jet separator or a split/split less injection port.

10.1.3 Surrogate and internal standard are added automatically by the Archon autosampler to every sample and standard except the BFB tune check. 1µL of the Working SIS solution is transferred to the Archon syringe containing the standard/sample prior to transfer to the concentrator.

10.2 **Initial calibration**. (periodic) Initial calibration standards must be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (See Tables 6a & 6b). Prepare these solutions in organic-free reagent water. At least one of the calibration standards must correspond to a concentration at or below the desired Method Reporting Limit. Typically, this method is calibrated at 1-150 µg/L for aqueous samples and 5-200 µg/L for soils. (Some compounds are higher). See Table 7 for example concentrations.

10.2.1 Prepare and analyze a tune check as in section 9.7.

10.2.2 A different calibration curve is necessary for aqueous and non-aqueous samples because of the differences in purging conditions. However, methanol extracts are analyzed against an aqueous curve.

10.2.3 The internal standards selected should permit most of the components of interest in a chromatogram to have retention times of 0.80 – 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation. If interferences are noted, use the next most intense ion as the quantitation ion.

10.2.4 Calculate response factors (RF) for each target analyte as described in Section 11. A system performance check should be made before this calibration curve is used.

Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum response factor. See below for SPCC criteria.

Compound	Minimum RF
Chloromethane	0.1
1,1,-Dichloroethane	0.1
Bromoform	0.1
Chlorobenzene	0.3
1,1,2,2,-Tetrachloroethane	0.3

These compounds are used to check for compound instability or check for degradation caused by contaminated lines or active sites in the system. Example problems include:

- Chloromethane is the most likely compound to be lost if the purge flow is too fast.
- Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve Bromoform response.
- Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

10.2.5 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration. See Section 11 for calculations. Typically the RSD will be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%.

- CCCs include the following compounds: 1,1-Dichloroethene, Chloroform, 1,2-Dichloropropane, Toluene, Ethylbenzene, and Vinyl Chloride. If samples are being analyzed for n-Hexane for OVAP, n-Hexane must also be evaluated as a CCC.
- If an RSD of greater than 30% is measured for any CCC, then the system is considered out-of-control and corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.
- If the CCCs are not included in the list of analytes for a project then all target compounds for that project must meet the same criteria as the CCCs or an RSD of less than or equal to 30%.

10.2.6 If the RSD of any target analyte is 15% or less, linearity through the origin can be assumed and the average response factor may be used to determine sample concentrations.

10.2.7 If the RSD for any analyte is greater than 15%, the analyst may wish to review the results for those analytes to ensure the problem is not associated with just one of the five to seven initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. It also may be necessary to narrow the calibration range.

10.2.8 If the RSD for any analyte is greater than 15% linearity through the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that does not pass through the origin. This approach may also be employed based on past experience or a prior knowledge of the instrument response. This is most easily achieved by performing a linear regression of the instrument response versus concentration of the standards. See Section 11 for linear regression calculations.

- The Enviroquant software is capable of generating a linear or quadratic plot. When this option is selected, care must be give to select the option that does not force the plot through the origin.
- The regression calculation will generate a correlation coefficient r that is a measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, r must be greater than or equal to 0.99. Enviroquant calculates r^2 which must be greater than or equal to 0.980.
- A quadratic or second order model may also be employed but at least six points must be used. In order to be used for quantitative purposes, r must be greater than or equal to 0.99. Enviroquant calculates r^2 which must be greater than or equal to 0.980. These curve fits can only be used for compounds that historically exhibit a non-linear response and can not be used to extend the calibration range for those compounds that normally exhibit a linear response but within a narrower calibration range.
- If the calibration fails to meet the linearity criteria, corrective action must be taken which may include reanalysis of a single standard or reanalysis of the entire calibration curve

10.2.9 Evaluation of retention times – The relative retention times of each target analyte in each calibration should agree within 0.06 relative retention time units.

10.2.10 Any sample analyzed following a calibration curve that does not meet the criteria addressed above must be re-analyzed with a valid calibration.

- If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag detections for the failing analyte in the affected samples.

10.2.11 <u>Low-level soil calibration</u>. The calibration described above is for aqueous samples. A separate calibration is required for low-level soil samples because purging is done at 40°C instead of the ambient temperature used for aqueous samples.

- Prepare calibration standards as described in Section 7 and Table 6b. Transfer 5 mL of the prepared standards to VOA vials containing either approximately 5g of clean matrix (such as sand) or 1g of of sodium bisulfate- depending upon the preservation condition of the samples. Cap the vial and seal tightly. It is essential that the vial be sealed properly because it is the actual purging vessel for soils. The standards are loaded onto the autosampler tray. DO NOT FILL THE VIAL COMPLETELY WITH STANDARD OR SAMPLE; THE ARCHON MUST ADD AN ADDITIONAL ALIQUOT OF WATER.
- The vial containing the standard is transferred to the soil sample cup where it is preheated at 40°C for 1.5 minutes. During this period, 5 mL of water is added to the vial with the surrogates and internal standards. When using the Archon autosampler, the purging of soils is performed in a VOA vial by the Archon and not in a fritted sparger tube connected to the concentrator. The standard is purged in the VOA vial for 11 minutes with helium (or nitrogen) to transfer the

volatile components from an aqueous phase to a vapor phase, at which point it is absorbed onto the sorbent trap in the concentrator.

- Once absorbed onto the trap, desorption, separation and detection are the same as described above for aqueous standards. The same calibration requirements are used for water and soil samples.

10.2.12 In some instances, it may not be practical to analyze a calibration curve in one 12-hour batch. Analysis of calibration standards may continue in a second batch providing no samples have been analyzed and analytical conditions have not changed.

10.3 **ICV** (Initial Calibration Verification) (moved from section 9)– The analysis of an independent reference standard or ICV is required following each curve. The ICV is prepared using the blank matrix as appropriate for samples that will be analyzed (reagent water, sand, sodium bisulfate- or other similar matrix) The Acceptance criteria is 60-140% recovery for analytes and surrogates, except for problematic compounds, which have a limit of 40-160%. If the limits are not met, the calibration curve must be reanalyzed. This standard may be used as an LCS when samples are analyzed in the same run batch. If used for an LCS, then the standard must meet the requirements described in section 9.5 This standard may also be used as a CCV.

10.3.1 If the ICV analyte (or surrogate) has a response that exceeds the recovery criteria, and the associated samples are non-detect for that analyte, then the sample data may be used without qualification and reanalysis is not required.

10.3.2 Problematic compounds are: Acrolein, acrylonitrile, 2-chloroethylvinyl ether, propionitrile, methylene chloride, 2-methynaphthalene and trans-1,4-dichloro-2-butene .

10.4 **CCV** (Continuing Calibration Verification) – Daily (moved from section 9)

10.4.1 The initial calibration curve must be verified for each compound of interest once every 12 hours prior to sample analysis. This is accomplished by analyzing a mid-point standard, typically 50-µg/L for waters or 50ug/Kg for soils, that contains all target compounds of interest. Acceptable CCV results must be obtained before any samples can be analyzed.

- The 50-µg/L standard included in the calibration curve may be used as a CCV in that run.
- If the CCV has a response that exceeds the recovery criteria, and the associated samples are non-detect for that analyte, then the sample data may be used without qualification and reanalysis is not required.

10.4.2 CCCs and SPCCs are evaluated against criteria in Table 5.

10.4.3 Surrogate acceptance criteria is 70-130% recovery.

10.4.4 Internal standards

- Response – If the EICP area for any of the internal standards in the CCV change 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.
- Retention Times - Retention times are affected by oven temperatures, column flow, length of column and other factors. The nature of this analysis is such that trimming length from the column is done on a routine basis to eliminate interferences and contaminants that may result from injection of samples. This

trimming results in a shorter column, therefore affecting retention time. The retention times of the internal standards in the CCV must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes unexpectedly by more than 30 seconds from that in the mid-point standard level in 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.

10.4.5 Evaluating the CCV for a short target list: If the CCCs are not included in the list of analytes for a project, and therefore are not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

10.4.6 Problems with CCVs may be due to standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, active sites/leaks in the column or purge and trap system or other analytical system issues. Problems may also be due to simple error in preparation of the standard.

10.4.7 Any sample analyzed after a CCV that failed any of the criteria above must be re-analyzed. If no sample is available for re-analysis, data must be flagged and the client notified of the deviation.

- If the CCV analyte has a response that exceeds the recovery criteria, and the associated samples are non-detect for that analyte, then th e sample data may be used without qualification and reanalysis is not required.

10.5 Aqueous sample analysis.

10.5.1 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

10.5.2 Temperature. Samples should be allowed to come to ambient temperature before analysis. Set up the introduction device as outlined above for standards.

10.5.3 The sample vial does not need to be opened in the laboratory for analysis. The autosampler is capable of removing a 5 mL (or other size) aliquot through the 40 mL vial septa (see above for introduction techniques). If headspace is present in the 40 mL vial, data collected must be flagged to indicate a potential loss of VOCs.

10.5.4 Dilutions. The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a 40 mL vial with no headspace.

- Dilutions may be made in 40 mL VOA vials.
  - 40 mL VOA vials hold 42 mL without headspace. Dilution volumes may be calculated based on this final 42 mL volume. Intermediate dilution steps may be necessary for extremely large dilutions.
  - Calculate the approximate volume of organic-free reagent water to be added to the VOA vial, and add slightly less than this quantity of organic-free reagent water to the vial.
  - Inject the appropriate volume of the original sample from an appropriate disposable or gas tight syringe into the vial. Add enough reagent water to remove any headspace, cap and invert several times to mix.
- Alternatively, dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

- Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.
- Inject the appropriate volume of the original sample from the syringe into the flask. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions. Transfer to a 40 mL VOA vial, ensuring no headspace is present.

10.5.5 Internal standard/surrogate. Internal standard and surrogate are automatically added by the autosampler with a final concentration of each at 50 µg/L or 50 µg/Kg. This may be done manually, but must be performed using the same technique for instrument and prep QC as for the samples.

10.5.6 Compositing aqueous samples prior to GC/MS analysis

- Add 10.5 mL of each sample to a 40 mL VOA vial, ensuring no headspace when four vials are composited. Add 7 mL of each sample to a 40 mL VOA vial when six vials are composited. Other volumes may be used, if equal volumes of each sample are composited.
- This process must be performed quickly to minimize volatilization losses. Dilutions can be performed on composited samples.
- Compositing samples for Volatiles analysis is not acceptable for OVAP.

10.5.7 MS/MSD. Select one sample from each run batch to be spiked with matrix spike. Add 4.2 µL each of VOA Primary Dilution Standard to two 40 mL VOA vials containing the sample to be spiked. If no sample is provided for an MS/MSD, the extra two VOA vials provided for sample analysis may be spiked once the sample has been successfully analyzed. If no sample is available to be used as an MS/MSD, then note in the appropriate log. Diluted samples may also be spiked for an MS/MSD (4.2 µL of VOA Primary Dilution Standard is added to two 40 mL VOA vials containing the diluted sample to be spiked). Other spike concentrations may be used.

10.5.8 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. See above for dilution techniques.

- Overcalibration results may be reported as estimated values, if approved by the client.

10.6 Low-level soil sample analysis.

10.6.1 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

10.6.2 Dilutions. Dilutions generally are not performed with low-level soils. A smaller aliquot of sample may be added to 5 mL of organic-free reagent water. If the sample contains a detection that exceeds the initial calibration range, a smaller aliquot of sample must be purged or a medium level sample preparation must be performed. The Archon cannot perform sample dilutions for soils.

- Overcalibration results may be reported as estimated values, if approved by the client.

10.6.3 MS/MSD. Select one sample from each run batch to be spiked with matrix spike and weigh in triplicate. Prepare a 20-µg/L standard as described above (5 µL of

VOA Primary Dilution Standard to 50mL of organic-free reagent water). Add 5 mL of the 20-µg/L standard to two of the sample aliquots for the MS/MSD. Final concentration is 20 µg/Kg. Other spike concentrations may be used.

10.7 Medium Level Soil Preparation/Analysis

10.7.1 A Method Blank, LCS and MS/MSD is extracted with each medium level extraction batch or one set for every 20 samples. The Method Blank is prepared by weighing 5 g of sand into a vial, adding 5 mL of methanol and sonicating for 2 minutes. Transfer 1 mL of the methanol to a VOA vial containing 41 mL of organic-free reagent water.

10.7.2 The medium level LCS is prepared by weighing 5 g of sand into a vial, adding 5 mL of methanol and 12.5 µL of the 8260 Medium Level LCS/MS/MSD spiking solution (2000 µg/mL) and sonicating for 2 minutes. Transfer 168 µL of the methanol extract to a VOA vial containing 42 mL of organic-free reagent water. The final concentration is 20 µg/mL. Other spike concentrations may be used.

10.7.3 The medium level MS/MSD is prepared by injecting 12.5 µL of the 8260 Medium Level LCS/MS/MSD spiking solution (2000 µg/mL) into a vial containing 5 g of sample and 5 mL of methanol. The extract is sonicated for 2 minutes and 168 µL of the extract is injected into a VOA vial containing 42 mL of organic-free reagent water. The final spike concentration is 20 µg/mL. The volume of the spiking solution added may be adjusted depending on the expected range of the target concentrations. Other spike concentrations may be used.

10.8 Qualitative analysis

The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions in a reference mass spectrum are defined to be 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. Compounds are identified as present when the following criteria are met.

10.8.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion. See **Table 10** for Estimated RTs and Quant Ions.

10.8.2 The relative retention time (RRT) of the sample component is within ±0.06 RRT units of the RRT of the standard component.

10.8.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

10.8.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. (m-Xylene and p-Xylene are examples of structural isomers that cannot be resolved and must be reported together.).

10.8.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by

more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

10.8.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

10.8.7 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

10.8.8 For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

- Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

10.9 Quantitative analysis

10.9.1 Once a compound is identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of a given analyte.

10.9.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor from the initial calibration data. See Section 11 for calculation details.

10.9.3 Where applicable, the concentration of any non-target analytes identified in the sample may be estimated. The sample formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

10.9.4 The resulting concentration should be reported indicating that the value is an estimate. Use the nearest internal standard free of interferences.

11.0 Calculations / Data Reduction

11.1 Response factors (RF)

$$RF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:

A_x = Area of characteristic ion for compound being measured.
C_{is} = Concentration of the specific internal standard.
A_{is} = Area of characteristic ion for the initial standard.
C_x = Concentration of the compound being measured.

11.2 Standard Deviation

SD = Standard Deviation of initial 5 RFs for each compound calculated as follows:

$$SD = \sqrt{\sum_{i=1}^{n} \frac{\left(x_i - \overline{x_i}\right)^2}{n-1}}$$

$\overline{x_i}$ = Mean (Average) of initial 5 RFs for each compound.

n = number of standards

x_i = individual RF

11.3 Relative Standard Deviation (%RSD)

$$\%RSD = \frac{SD}{RF} \times 100$$

where:

RF = The average of the 5 or more initial calibration RFs
SD = The standard deviation of the average RFs

11.4 **Linear regression calculation**

This calculation is used when the %RSD exceeds 15%.

$$Y = ax + b$$

where:

Y = Instrument response (total area sum)
a = Slope of the line (coefficient of x)
x = Concentration of calibration standard
b = The intercept

The Enviroquant data system is capable of generating a linear plot. The analyst should not force the line through the origin.

11.5 The mathematics used in least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves generated tend to fit points at the upper calibration levels better than points at the lower calibration levels. To compensate for this, a weighting factor which reduces this tendency is used. Examples of acceptable weighting factors which place more emphasis on numbers of smaller value are:

$w = 1/y$ or $w = 1/y^2$

11.6 **Coefficient of Determination**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2}$$

Correlation Coefficient

$$r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response
x = Concentration

11.7 **Percent Difference (%D)**

$$\%D = \frac{[RF_{ave} - RF_c]}{[RF_{ave}]} \times 100$$

where:

RF_{ave}= The average of the 5 or more initial calibration RFs
RF_c = Continuing calibration RF

11.8 **% Drift Calculation**

% Drift calculation in used for comparing continuing calibration responses to a **linear** curve. The criteria for % Drift is the same as for % Difference.

$$\%Drift = \frac{\text{Calculated concentration - Theoretical concentration}}{\text{Theoretical concentration}} \times 100\%$$

11.9 **Concentration of Water and Water-miscible waste**

$$\text{Conc. } (\mu g/L) = \frac{C\ (5.0\ mL)}{(V)}$$

Where:
C = concentration reported by the data system.
V = Volume of sample purged (mL) taking into consideration any dilutions.

11.10 **Concentration of Volatiles in Low Level Soil/Sediment samples:**

$$\text{Conc. } (\mu g/Kg) = \frac{C\ (5.0\ mL)}{(W)\ (S)}$$

Where:

C = Concentration reported by the data system (See 9.5).
W = Wet Weight of sample extracted, grams
S = Solid fraction, % solids/100

11.11 **Concentration of Volatiles in Medium Level Soil/Sediment:**

$$\text{Conc. } (\mu g/Kg) = \frac{C\,(V_t)\,(5.0\text{ mL})}{(V_i)(W)\,(S)}$$

Where:

C	=	Concentration reported by the data system.
W	=	Wet Weight of sample extracted, grams
S	=	Solid fraction, % solids/100
V_i	=	Volume of extract added (µL) for purging
V_t	=	Volume of total extract (µL)

11.12 **Surrogate % Recovery**

$$\%\text{ Recovery} = \frac{\text{Concentration detected}}{\text{Concentration spiked}} \times 100$$

11.13 **Matrix Spike/Matrix Spike Duplicate (MS/MSD) Percent Recovery or LCS Percent Recovery:**

$$\%\text{Recovery} = \frac{(S-U)}{T} \times 100$$

Where:

S	=	Spiked result
U	=	Unspiked result (use 0 for LCS)
T	=	Spike True Concentration

11.14 **Relative Percent Difference (RPD) of Matrix Spikes**

$$\text{RPD} = \frac{(\text{Larger value} - \text{Smaller Value})}{(\text{Average of the Values})} \times 100$$

12.0 Method Performance

12.1 The supervisor has responsibility to ensure that an analyst who has been performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilitie s - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study – A method detection limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted in a manner consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.2 The following waste streams are produced when this method is carried out:

- Aqueous waste generated from analysis. This material may have a pH of less than 2.0. The wastes is neutralized and discharged into the sanitary sewer.
- Solvent waste generated from analysis, is collected, drummed, and disposed of through a Waste Handler.
- Solid waste generated from analysis is disposed of in general trash
- Expired standards are treated as Solvent Waste

15.0 References / Cross-References

15.1 "Test Methods for Evaluating Solid Waste" EPA, 3rd Edition, Final Update I, Revision 1, 7/1992, Method 5030A

15.2 "Test Methods for Evaluating Solid Waste" EPA, 3rd Edition, Update II, Revision 1, 9/1994, Method 8260A

15.3 "Test Methods for Evaluating Solid Waste" EPA, 3rd Edition, Update III, Revision 2, 12/1996, Methods 5000, 5030B, 5035A, 8000B, and 8260B.

15.4 DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton

15.5 DT-QA-005 Procedure for Balance Calibration Check

15.6 DT-QA-006 Thermometer Calibration

15.7 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.

15.8 This is an OVAP approved SOP. All changes must be approved by OVAP prior to implementation.

16.0 Method Modifications

SOP Section	Method	Modification	Justification
7	SW 8260B	Do not allow standard solutions to warm to room temperature.	Volatile standards are subject to rapid decomposition under warmer temperatures. To extend the life of the standards, they are

			typically used without bringing to room temperature.
7	Standards for Gases good for one week.	Standards for gases are prepared monthly.	We monitor the gases daily through analysis of the CCV. Vinyl Chloride, a CCC, is a gas. When the response begins to drop off we replace the standard- or at least monthly.

17.0 Attachments

Table 1 Example Method Reporting Limits
Table 2 Preparation of Calibration Primary Dilution Standard
Table 3 Preparation of ICV/LCS Primary Dilution Standard
Table 4 BFB Mass Intensity Criteria
Table 5 SPCC and CCC Calibration and CCV Criteria
Table 6a Aqueous Calibration Standard Preparation
Table 6b Non- Aqueous Calibration Standard Preparation
Table 7 Concentrations of Calibration Standards, µg/L
Table 8 Recommended Purge-and-Trap Operating Conditions
Table 9a Recommended GC/MS Operating Conditions for the 5890/5970
Table 9b Recommended GC/MS Operating Conditions for the 6980/5973
Table 10 Estimated RTs, and Quant Ions

18.0 Revision History

18.1 Revision Dates

3/31/11 Biannual Review
8/30/07

18.2 Changes from last revision

Item	Change from	Change to	Reason
Copyright	2007 info	2011 info	Copyright is updated annually.
Section 1.1	Added	This method is restricted to use by or under the supervision of an alysts experienced in the use o f gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra.	Clarification and consistency with other chromatographic SOPs.
Section 1.2	Added	For the purposes of this procedure, 8260A and 8260B are distinguished by the sampling technique used to collect the samples. All waters may be reported by 8260B. If soils are collected in a manner consistent with 5035A, then they may be reported by 8260B, otherwise they are reported as 8260A.	Clarification of procedure.

Item	Change from	Change to	Reason
Section 1.3.1	Added	Additional compounds may be analyzed using this procedure, provided all appropriate quality control measures are evaluated and found acceptable. For OVAP, only compounds listed in the method may be reported using this procedure (with the exception of n-Hexane which requires specific certification)	Clarification of procedure.
4.7	Added	If recovery failures occur, possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, active sites/leaks in the column or purge and trap system.	Clarification of procedure.
7.4	Added	Other amounts of BFB may be used, but the amount injected onto column must be less than or equal to 50 ng.	Clarification of procedure.
7.6.3.1	Added	It is acceptable to prepare separate calibration curves for additional analytes- for example, Tetrahydrofuran is not part of the typical daily calibration. If analysis is requested, a separate calibration is analyzed.	Clarification of procedure.
7.6.7.1	Added	Manual addition of the surrogates and internal standards is acceptable, but manual or automatic- the procedure must be the same for calibration and other QC as for the samples.	Clarification of procedure.
7.8.	5035A low level soil ICV should be added to a vial containing 1g of sodium bisulfate …	5035A low level soil ICV should be added to a vial containing 1g of sodium bisulfate …**or 5g clean sand- depending on how the calibration was prepared.**	Clarification of procedure.
7.8	An ICV should be analyzed with all initial calibrations to verify the calibration.	An ICV <u>must</u> be analyzed with all initial calibrations to verify the calibration. <u>The ICV may be prepared at other concentrations within the calibrated range.</u>	Clarification of procedure and provide acceptable caveat.
7.9	Added	… The LCS may be prepared at other concentrations within the calibrated range.	Clarification of procedure and provide acceptable caveat.
7.10	Added	… . The CCV may be prepared at other concentrations within the calibrated range.	Clarification of procedure and provide acceptable caveat.
8.0	Added	OVAP and most other environmental samples require compliance with the	Clarification requested by

Item	Change from	Change to	Reason
		information detailed in the analytical methods.	OVAP.
9.3.4	Added	If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag detections for the failing analyte in the affected samples, LCS, MS/MSD with a "B". For OVAP, provide an explanation in the QC narrative.	Clarification of procedure and provide acceptable caveat.
9.4	Added	… also extracted with each Medium Level extraction. **Other spike concentrations may be used.** Any samples analyzed…	Clarification of procedure and provide acceptable caveat.
9.4.1, 9.4.2, 9.4.3	Added	The LCS may be spiked with and/or evaluated for a limited list of target analytes, provided this is acceptable to the regulatory program for which samples are being analyzed. If the LCS fails to meet criteria, then the extraction batch is considered out-of-control for the compounds that failed for all associated samples, and re-extraction/re-analysis for those compounds must be performed before results are reported If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag detections for the failing analyte in the affected samples, LCS and Method Blanks, do not flag the MS/MSD. For OVAP, provide an explanation in the QC narrative.	Clarification of procedure and provide acceptable caveat.
9.4.4	Removed	If the LCS recovery is high and the associated samples are <MRL, reanalysis is not required, ~~but data must be flagged.~~	As there is no negative impact on the data, flagging may not be necessary, based on client and agency needs.
9.5.1	Added	Only those surrogates associated with the analytes of interest need to be spiked and/or evaluated.	Clarification of procedure.
9.5.4 bullets	Added	If the Method Blank or LCS has high surrogate recovery, and the samples are non-detect for the associated analytes, then reanalysis of the Method Blank or LCS is not necessary.	Clarification of procedure.

Item	Change from	Change to	Reason
		If there is an obvious matrix effect as evidenced by chromatography, sample foaming, or other physical matrix issue, re-extraction is not required. Flag surrogate recovery in the individually affected samples, MS/MSD. For OVAP, provide an explanation in the QC narrative. If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag surrogate recovery in the individually affected samples, Method Blank, LCS, MS/MSD. For OVAP, provide an explanation in the QC narrative.	
9.6.1	Added	The MS/MSD may be evaluated for a limited list of target analytes, provided this is acceptable to the regulatory program for which samples are being analyzed.	Clarification of procedure and provide acceptable caveat.
9.6.2	The MS/MSD must meet the same recovery criteria outlined in the Control Limits Manual. The RPD between the replicates must be <25%. See Section 11 for percent recovery and RPD calculations.	The MS/MSD acceptance criteria is maintained in LIMS. See Section 11 for percent recovery and RPD calculations.	Limits are no longer maintained in a Control Limits Manual.
9.6.5	If insufficient sample has been provided for a MS/MSD then the data must be flagged with a narrative.	If insufficient sample has been provided for a MS/MSD then make a note in the appropriate raw data or logbook.	Procedure is changed, flagging of data is no longer necessary.
9.8.2 bullets	A single scan at the Apex (only) may also be used for the evaluation of the tune An average across the entire	A single scan at the Apex (only) may also be used for the evaluation of the tune, **background correction is still required.** ~~An average across the entire peak may be used. Background subtraction is not required. This is consistent with EPA Method 524.~~	Corporate policy does not allow for this tune procedure.

Item	Change from	Change to	Reason
	peak may be used. Background subtraction is not required. This is consistent with EPA Method 524.		
9.9.2, 9.9.3, 9.9.4, 9.9.5	Added	For OVAP, samples must not be reported with failing internal standards. If there is potential for the direct analysis of the sample to cause harm to the analytical system, such as when a sample is foamy, or suspected to contain high levels of analyte or non-target contamination, then initial analysis of the sample may be performed at a dilution. If a matrix effect is determined <u>to impact the internal standards, the sample must be diluted or processed in another manner to</u> bring the internal standard recoveries into limits. Matrix interference may be apparent through chromatographic evidence or sample color, foaming or other physical characteristic. Excessive dilution to correct recoveries at the expense of removing target analytes is not acceptable.	Clarify OVAP requirements.
9.10.2	Added	On rare occasions, a sample result that is slightly above calibration will result in a value that is slightly below calibration when analyzed at a methanol extraction. In these cases, it may be appropriate to report both results with appropriate flags and/or a narrative.	Clarification of procedure.
9.11	Added	For Ohio VAP: The laboratory must implement corrective action procedures to resolve the deviation and limit qualification of the final results. The laboratory is not permitted to deviate from its VAP approved SOP if it intends to attest under affidavit that the "results" are VAP certified. When all corrective actions listed in the SOP have been exhausted, it may be necessary to use technical judgment in which case the	Clarify OVAP requirements.

Item	Change from	Change to	Reason
		decision process and rationale will be presented in the final report and/or affidavit **and the data will be noted as 'not VAP certified' on the affidavit.**	
10.2.8 bullet 3	Added	… These curve fits can only be used for compounds that historically exhibit a non-linear response….	Clarification of procedure.
10.2.10	Added	… If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag detections for the failing analyte in the affected samples…	Clarification of procedure and provide acceptable caveat.
10.4.3	Added	Surrogate acceptance criteria is 70-130% recovery.	Define surrogate recovery criteria in CCVs.
10.5	Removed	Sample integrity. The process of taking an aliquot destroys the validity of the remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Aliquots should not be removed from a sample vial that has the septa pierced and headspace present.	This procedure is not used at the laboratory.
10.5.4	Removed	Alternatively, the Archon autosampler can perform sample dilutions of 2X, 5X, 10X, 20X, 50X and 100X without opening the VOA vial. Organic-free reagent water is provided for the dilution via a reservoir attached to the autosampler.	This dilution technique has been shown to be unreliable, and is not used at the laboratory.
10.5.5	Added	… This may be done manually, but must be performed using the same technique for instrument and prep QC as for the samples.	Clarification of procedure and provide acceptable caveat.
10.5.6 bullet 3	Added	Compositing samples for Volatiles analysis is not acceptable for OVAP.	Clarify OVAP requirements.
10.5.7	Added	… Other spike concentrations may be used.	Clarification of procedure and provide acceptable caveat.
10.5.8 bullet	Added	Over-calibration results may be reported as estimated values, if approved by the client.	Clarification of procedure and provide acceptable caveat.

Item	Change from	Change to	Reason
Section 15	Added	DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton DT-QA-005 Procedure for Balance Calibration Check DT-QA-006 Thermometer Calibration DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus. This is an OVAP approved SOP. All changes must be approved by OVAP prior to implementation.	Information in these documents is used daily in processing samples with this SOP.
Table 1 Notes	Added	*- these compounds are not listed in method 8260 and can not be reported for OVAP (excluding Hexane that can be reported but only when certain QC criteria are met) ** these compounds are listed in method 8260, but are not part of our typical target analyte list. If analysis is performed for these it typically requires a separate calibration.	Clarification of procedure and provide acceptable caveat.
Table 2 Notes	Added	NOTE: Other vendors/concentrations may be used, and other volumes of standards may be prepared. Consider initial concentrations and final volumes in all standard calculations.	Clarification of procedure and provide acceptable caveat.
Table 3 Notes	Added	NOTE: Other vendors/concentrations may be used, and other volumes of standards may be prepared. Consider initial concentrations and final volumes in all standard calculations.	Clarification of procedure and provide acceptable caveat.
Table 4 Notes	Added	NOTE: The intensity requirements are in whole #s, as such the acceptance is evaluated in whole #s. For example, m/z 50 recovered at 14.7% (required intensity is 15 to 40% of m/z 95) is acceptable. The data system may tag this as failing. The analyst should note on the data that it is acceptable.	Clarification of procedure.

Item	Change from	Change to	Reason
Table 6a Notes	Added	NOTE: If the concentration of the Primary Dilution Standard is changed, then the volume used and final volumes for the Calibration Standards must be changed accordingly. The Method Reporting Limit must be supported by a concentration point in the curve.	Clarification of procedure and provide acceptable caveat.
Table 6b Notes	Added	NOTE: If the concentration of the Primary Dilution Standard is changed, then the volume used and final volumes for the Calibration Standards must be changed accordingly. The Method Reporting Limit must be supported by a concentration point in the curve.	Clarification of procedure and provide acceptable caveat.
Table 7 Notes	Added	NOTE: If the concentration of the lowest Calibration standard changes, then the MRLs must be adjusted accordingly.	Clarification of procedure.
Entire document	Changed	Blank, as it refers to Method Blank, was changed to Method Blank.	OVAP requirement, consistency
Entire document	Changed	RL, as it refers to Method Reporting Limits, was changed to MRL	OVAP requirement, consistency

Table 1: Example Method Reporting Limits

Analyte	Water MRL (ug/L)	Soil MRL (ug/Kg)
Acetone	20	100
Acrolein	50	50
Acrylonitrile	50	50
Allyl chloride	5	5
tert-Amyl Methyl Ether*	1	5
Benzene	1	5
tert-Butyl acetate **		
tert-Butylbenzene	1	5
sect-Butylbenzene	1	5
n-Butylbenzene	1	5
Bromochloromethane	1	5
Bromodichloromethane	1	5
Bromoform	1	5
Bromobenzene	1	5
Bromomethane	5	10
tert-Butyl Alcohol **		
2-Butanone (MEK)	10	50
Carbon disulfide	1	5
Carbon tetrachloride	1	5
Chlorobenzene	1	5
Chloroethane	5	10
2-chlorotoluene	1	5
4-chlorotoluene	1	5
Chloroform	1	5
2-chloroethylviny ether	5	5
Chloromethane	5	10
Chloroprene	5	5
Cylohexane *	5	5
Dibromochloromethane	1	5
Dibromomethane	1	5
Dichlorodifluoromethane	1	5
1,2-Dibromo-3-chloropropane	5	5

1,2-Dibromoethane (EDB)	5	5
1,2-Dichlorobenzene	1	5
1,3-Dichlorobenzene	1	5
1,4-Dichlorobenzene	1	5
trans-1,4-Dichloro-2-butene	5	5
1,1-Dichloroethane	1	5
1,2-Dichloroethane	1	5
1,1-Dichloroethene	1	5
cis-1,2-Dichloroethene	1	5
trans-1,2-Dichloroethene	1	5
Dichlorofluoromethane **		
Dichloromethane	5	5
1,2-Dichloropropane	1	5
1,3-Dichloropropane	1	5
2,2-Dichloropropane	1	5
1,1-Dichloropropene	1	5
cis-1,3-Dichlorpropene	1	5
trans-1,3-Dichloropropene	1	5
Diisopropyl ether (IPE) *		
Ethylbenzene	1	5
Ethyl methacrylate	5	5
Ethyl ether	5	5
Ethyl acetate	5	20
Ethyl tert-butyl ether (ETBE) *		
Hexachlorobutadiene	5	5
n-Hexane *	5	10
2-Hexanone	10	50
Iodomethane	5	5
Isopropylbenzene	1	5
p-Isopropyltoluene	1	5
Methacrylonitrile	5	5
Methyl acetate **		
Methyl cyclohexane **		
2-Methylnaphthalene *	5	5
tert- Butyl Methyl Ether (MTBE)	1	5
4-Metyl-2-pentanone (MIBK)	10	50

Methyl methacrylate	5	5
2-Nitropropane **		
Pentachloroethane	5	5
Propionitrile	50	50
n-Propylbenzene	1	5
Styrene	1	5
Naphthalene	5	5
1,1,1,2-Tetrachloroethane	1	5
1,1,2,2-Tetrachloroethane	1	5
Tetrachloroethene	1	5
Tetrahydrofuran **		
Toluene	1	5
1,2,4-Trichlorobenzene	5	5
1,2,3-Trichlorobenzene	5	5
1,1,1-Trichloroethane	1	5
1,1,2-Trichloroethane	1	5
Trichloroethene	1	5
1,2,3-Trichloropropane	1	5
Trichlorofluoromethane	1	5
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113) *		
1,2,4-Trimethylbenzene	1	5
1,3,5-Trimethylbenzene	1	5
Vinyl acetate	5	5
Vinyl chloride	1	2
m&p- Xylene	2	5
o-Xylene	1	5

NOTE: *- these compounds are not listed in method 8260 and can not be reported for OVAP (excluding Hexane that can be reported but only when certain QC criteria are met)

NOTE: ** these compounds are listed in method 8260, but are not part of our typical target analyte list. If analysis is performed for these it typically requires a separate calibration.

Table 2: Preparation of Calibration Primary Dilution Standard

Vendor	Product #	Name	Conc. (µg/mL)	Volume
Restek	30633	8260B Cal Mix 1	2000	1 mL
Restek	30265	2-chloroethylvinyl ether	2000	1 mL
Restek	30646	Acrolein Mix	5,000	2 mL
Restek	30042	502.2 Calibration Mix 1	2000	1 mL
Restek	30216	Vinyl Acetate Standard	2000	1 mL
Restek	30006	VOA Calibration Mix 1	5000	1 mL
Restek	552135	Custom Revised Volatiles Standard	2000-4000	1 mL
Fisher		Purge and Trap Methanol	NA	2 mL

NOTE: Other vendors/concentrations may be used, and other volumes of standards may be prepared. Consider initial concentrations and final volumes in all standard calculations.

Table 3: Example Preparation of ICV/LCS Primary Dilution Standard

Vendor	Product #	Name	Conc. (µg/mL)	Volume
Supelco	502111	502/524 Volatiles Cal Mix	2000	1 mL
Supelco	86-1145	Chloroprene	2,000	1 mL
Supelco	5-06052	Iodomethane	2000	1 mL
NSI	327-06-06	Vinyl Acetate Standard	2000	1 mL
Supelco	86-1206	2-Chloroethyl vinyl ether	2000	1 mL
Supelco	48799-U	VOC Mix 6	2000	1 mL
Supelco	46871-U	Acrolein/Acrylonitrile	10,000	1 mL
Supelco	86-1208	Cal Mix 2A	2000	1 mL
Ultra Scientific	C45-10547	Custom Standard	2000-5000	1 mL
Fisher		Purge and Trap Methanol	NA	1mL

NOTE: Other vendors/concentrations may be used, and other volumes of stand ards may b e prepared. Consider initial concentrations and final volumes in all standard calculations.

Table 4: BFB Mass Intensity Criteria

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% 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

NOTE: The intensity requirements are in whole #s, as such the acceptance is evaluated in whole #s. For example, m/z 50 recovered at 14.7% (required intensity is 15 to 40% of m/z 95) is acceptable. The data system may tag this as failing. The analyst should note on the data that it is acceptable.

Table 5: SPCC and CCC Calibration and CCV Criteria

SPCCs:

Compound	Minimum RF
Chloromethane	0.1
1,1,-Dichloroethane	0.1
Bromoform	0.1
Chlorobenzene	0.3
1,1,2,2,-Tetrachloroethane	0.3

CCCs:

Compound	Maximum RSD	Maximum % Drift
1,1-Dichloroethene	30%	20%
Chloroform	30%	20%
1,2-Dichloropropane	30%	20%
n-Hexane (only when an OVAP target)	30%	20%
Toluene	30%	20%
Ethylbenzene	30%	20%
Vinyl chloride	30%	20%

Table 6a: Example Aqueous Calibration Standard Preparation

Calibration Level	*Volume of Primary Dil. Standard (µL)*	*Volume of Organic-free Reagent water (mL)*
1 ppb	1 µL	200 mL
4 ppb	4 µL	200 mL
10 ppb	5 µL	100 mL
20 ppb (LCS)	5 µL	50 mL
50 ppb (CCV)	12.5 µL	50 mL
100 ppb	25 µL	50 mL
150 ppb	37.5 µL	50 mL

NOTE: If the concentration of the Primary Dilution Standard is changed, then the volume used and final volumes for the Calibration Standards must be changed accordingly.

The Method Reporting Limit must be supported by a concentration point in the curve.

Table 6b: Example Non-Aqueous Calibration Standard Preparation

Calibration Level	*Volume of Primary Dil. Standard (µL)*	*Volume of Organic-free Reagent water (mL)*
2 ppb	2 µL	200 mL
5 ppb	5 µL	200 mL
10 ppb	5 µL	100 mL
20 ppb (LCS)	5 µL	50 mL
50 ppb (CCV)	12.5 µL	50 mL
100 ppb	25 µL	50 mL
150 ppb	37.5 µL	50 mL
200 ppb	50 µL	50 mL

NOTE: If the concentration of the Primary Dilution Standard is changed, then the volume used and final volumes for the Calibration Standards must be changed accordingly.

The Method Reporting Limit must be supported by a concentration point in the curve.

Table 7: Concentrations of Calibration Standards, µg/L

	Standard									
	1	***2***	***4***	***5***	***10***	***20***	***50***	***100***	***150***	***200***
Compound										
Acetone	2.5	5	10	12.5	25	50	125	250	375	500
Acrolein	10	20	40	50	100	200	500	1000	1500	2000
Acrylonitrile	1	2	4 5		10	20	50	100	150	200
Allyl chloride	1	2	4	5	10	20	50	100	150	200
Benzene	1	2	4	5	10	20	50	100	150	200
tert-Butylbenzene	1	2	4	5	10	20	50	100	150	200
sec-Butylbenzene	1	2	4	5	10	20	50	100	150	200
n-Butylbenzene	1	2	4	5	10	20	50	100	150	200
Bromochloromethane	1	2	4	5	10	20	50	100	150	200
Bromodichloromethane	1	2	4	5	10	20	50	100	150	200
Bromoform	1	2	4	5	10	20	50	100	150	200
Bromobenzene	1	2	4	5	10	20	50	100	150	200

Bromomethane	1	2	4 5		10	20	50	100	150	200
2-Butanone (MEK)	2.5	5	10	12.5	25	50	125	250	375	500
Carbon Disulfide	1	2	4	5	10	20	50	100	150	200
Carbon tetrachloride	1	2	4	5	10	20	50	100	150	200
Chlorobenzene	1	2	4	5	10	20	50	100	150	200
Chloroethane	1	2	4	5	10	20	50	100	150	200
2-Chlorotoluene	1	2	4	5	10	20	50	100	150	200
4-Chlorotoluene	1	2	4	5	10	20	50	100	150	200
Chloroform	1	2	4	5	10	20	50	100	150	200
2-chloroethylvinyl ether	1	2	4	5	10	20	50	100	150	200
Chloromethane	1	2	4	5	10	20	50	100	150	200
Chloroprene	1	2	4	5	10	20	50	100	150	200
Dibromochloromethane	1	2	4	5	10	20	50	100	150	200
Dibromomethane	1	2	4 5		10	20	50	100	150	200
Dichlorodifluoromethane	1	2	4 5		10	20	50	100	150	200
1,2-Dibromo-3-chloropropane	1	2	4 5		10	20	50	100	150	200
1,2-Dibromoethane (EDB)	1	2	4	5	10	20	50	100	150	200
1,2-Dichlorobenzene	1	2	4 5		10	20	50	100	150	200
1,3-Dichlorobenzene	1	2	4 5		10	20	50	100	150	200
1,4-Dichlorobenzene	1	2	4 5		10	20	50	100	150	200
trans-1,4-Dichloro-2-butene	1	2	4 5		10	20	50	100	150	200
1,1-Dichloroethane	1	2	4 5		10	20	50	100	150	200
1,2-Dichloroethane	1	2	4 5		10	20	50	100	150	200
1,1-Dichloroethene	1	2	4 5		10	20	50	100	150	200
cis-1,2-Dichloroethene	1	2	4 5		10	20	50	100	150	200
trans-1,2-Dichloroethene	1	2	4 5		10	20	50	100	150	200
Dichloromethane	1	2	4 5		10	20	50	100	150	200
1,2-Dichloropropane	1	2	4 5		10	20	50	100	150	200
1,3-Dichloropropane	1	2	4 5		10	20	50	100	150	200
2,2-Dichloropropane	1	2	4 5		10	20	50	100	150	200
1,1-Dichloropropene	1	2	4 5		10	20	50	100	150	200
cis-1,3-Dichloropropene	1	2	4 5		10	20	50	100	150	200
trans-1,3-Dichloropropene	1	2	4 5		10	20	50	100	150	200
Ethylbenzene	1	2	4 5		10	20	50	100	150	200
Ethyl methacrylate	1	2	4	5	10	20	50	100	150	200

Ethyl ether	1	2	4	5	10	20	50	100	150	200
Ethyl Acetate	2	4	8	10	20	40	100	200	300	400
Hexachlorobutadiene	1	2	4 5		10	20	50	100	150	200
n-Hexane	2	4	8	10	20	40	100	200	300	400
2-Hexanone	2.5	5	10	12.5	25	50	125	250	375	500
Iodomethane	1	2	4 5		10	20	50	100	150	200
Isopropylbenzene	1	2	4 5		10	20	50	100	150	200
p-Isopropyltoluene	1	2	4 5		10	20	50	100	150	200
Methacrylonitrile	1	2	4 5		10	20	50	100	150	200
2-Methylnaphthalene	1	2	4 5		10	20	50	100	150	200
tert-Butyl Methyl Ether (MTBE)	1	2	4	5	10	20	50	100	150	200
4-Methyl-2-pentanone (MIBK)	2.5	5	10	12.5	25	50	125	250	375	500
Methyl methacrylate	1	2	4	5	10	20	50	100	150	200
Pentachloroethane	1	2	4	5	10	20	50	100	150	200
Propionitrile	3	6	12	15	30	60	150	300	450	600
n-Propylbenzene	1	2	4	5	10	20	50	100	150	200
Styrene	1	2	4 5		10	20	50	100	150	200
Naphthalene	1	2	4	5	10	20	50	100	150	200
1,1,1,2-Tetrachloroethane	1	2	4	5	10	20	50	100	150	200
1,1,2,2-Tetrachloroethane	1	2	4	5	10	20	50	100	150	200
Tetrachloroethene	1	2	4	5	10	20	50	100	150	200
Toluene	1	2	4	5	10	20	50	100	150	200
1,2,4-Trichlorobenzene	1	2	4	5	10	20	50	100	150	200
1,2,3-Trichlorobenzene	1	2	4	5	10	20	50	100	150	200
1,1,1-Trichloroethane	1	2	4	5	10	20	50	100	150	200
1,1,2-Trichloroethane	1	2	4	5	10	20	50	100	150	200
Trichloroethene	1	2	4	5	10	20	50	100	150	200
1,2,3-Trichloropropane	1	2	4	5	10	20	50	100	150	200
Trichlorofluoromethane	1	2	4	5	10	20	50	100	150	200
1,2,4-Trimethylbenzene	1	2	4	5	10	20	50	100	150	200
1,3,5-Trimethylbenzene	1	2	4	5	10	20	50	100	150	200
Vinyl Acetate	1	2	4	5	10	20	50	100	150	200
Vinyl chloride	1	2	4	5	10	20	50	100	150	200
m&p-Xylene	2	4	8	10	20	40	100	200	300	400
o-Xylene	1	2	4	5	10	20	50	100	150	200

NOTE: If the concentration of the lowest Calibration standard changes, then the MRLs must be adjusted accordingly.

Table 8: Recommended Purge-and-Trap Operating Conditions

TekMar Transfer Line Temperature	135°C
TekMar 6-port Valve Temperature	135°C
TekMar Mount Temperature	40°C
Archon Transfer Line Temperature	110°C
Archon Valve Temperature	110°C
Archon Probe Temperature	95°C
Archon Preheat Temperature	40°C
Archon Preheat Time	3 min
Purge Volume (aqueous)	5 mL
Purge Ready Temperature	<35°C
Purge Flow	40mL/min
Purge Time	11 min
Dry Purge Time	2 min
Desorb Preheat Temperature	245°C
Desorb Temperature	250°C
Desorb Time	2 min
Bake Time	8 min
Bake Temperature	270°C
Trap	Vocarb 3000

Table 9a: Recommended GC/MS Operating Conditions for the 5890/5970:

Column flow	8-12 ml/min
Detector A (Jet Separator) Temperature	250 ^{o}C
Detector B (GC/MS Interface) Temperature	250 ^{o}C
Column:	J&W DB-624 75 M X 0.53 mm x 3.0 um
Oven Program:	
Initial Temperature	35 ^{o}C
Initial Time	5.00 min
Ramp Program Rate	7 ^{o}C/min
Ramp1 Final Temperature	70 ^{o}C
Ramp 1 Final Time	0.00 min
Ramp 2 Program Rate	13 ^{o}C/min
Ramp 2 Final Temperature	220 ^{o}C
Ramp 2 Final Time	1.50 min or greater
MS Threshold	500
Mass range	35-300 amu
Scan time	To give 5 scans/peak but not to exceed 5 sec/scan
Sample #	3
A/D Samples	8
BFB Oven Program:	
Initial Temperature	70 ^{o}C
Ramp Program Rate	13 ^{o}C/min
Ramp1 Final Temperature	220 ^{o}C
Ramp 1 Final Time	0.00 min

Table 9b: Recommended GC/MS Operating Conditions for the 6890/5973

Front inlet:	
Mode:	Split
Initial Temperature:	250 ^{o}C
Pressure:	18.9 psi
Split ratio:	15:1
Split flow:	17.4 ml/min
Total Flow:	21.3 ml/min
Gas Saver:	On
Saver Flow:	174.0 ml/min
Saver Time:	0.75 min
Gas Type:	Helium (or nitrogen)
Column:	J&W DB-624 25 M X 0.2 mm x 1.14 um
Mode:	Constant flow
Oven :	
Initial Temperature:	35 ^{o}C
Initial Time	5.00 min
Ramp 1 Program Rate	35°C/min
Ramp 1 Final Temperature	45 ^{o}C
Ramp 1 Final time	4.71 min
Ramp 2 Program Rate	12 ^{o}C/min
Ramp 2 Final Temperature	190 ^{o}C
Ramp 2 Final Time	0 min
Ramp 3 Program Rate	25 ^{o}C/min
Ramp 3 Final Temperature	220 ^{o}C
Ramp 3 Final Time	0 min
MS Threshold	500
Mass range	35-300 amu
Scan time	To give 5 scans/peak but not to exceed 5 sec/scan
Sample #	3
A/D Samples	8
MS Quad Temperature	150 ^{o} C
MS Source Temperature	230 ^{o} C

MSD Transfer line Temperature	260 ^{o} C
BFB Oven Program:	
Initial Temperature	70 ^{o}C
Ramp Program Rate	13 ^{o}C/min
Ramp1 Final Temperature	220 ^{o}C
Ramp 1 Final Time	0.0 min

Table 10: Example RTs and Quant Ions

	Compound	RT	Quant Ion	Secondary Ions		
1	Fluorobenzene- ISTD	6.526	96	70		
2	Dichlorodifluoromethane	1.217	85	87		
3	Chloromethane	1.379	50	52		
4	Vinyl Chloride	1.463	62	64		
5	Bromomethane	1.761	94	96		
6	Chloroethane	1.855	64	66		
7	Ethyl Ether	2.373	59	45	74	
8	Trichlorofluoromethane	2.059	101	103		
9	Acrolein	2.582	56	55		
10	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	2.582	151	153	101	103
11	Acetone	2.765	58	43		
12	1,1-Dichloroethene	2.609	96	61	63	
13	Allyl Chloride	3.074	41	39	76	
14	Methyl Iodide (Iodomethane)	2.786	142	127		
15	Acrylonitrile	3.749	53	52		
16	Methylene Chloride	3.278	84	49	86	
17	Carbon Disulfide	2.813	76	78		
18	trans 1,2-Dichloroethene	3.581	96	61	98	
19	Methyl t-butyl ether	3.581	73	57		
20	1,1-Dichloroethane	4.303	63	65	83	
21	Hexane	3.890	57	56	41	43
22	Chloroprene	4.376	53	88	51	
23	Vinyl Acetate	4.423	86	43		
24	2-Butanone (MEK)	5.234	72	43		
25	cis 1,2-Dichloroethene	5.145	96	61	98	
26	Propionitrile	5.407	54	55		

27	Ethyl Acetate	5.286	45	43	88	
28	Methacrylonitrile	5.543	41	39	67	52
29	Bromochloromethane	5.459	128	130	49	
30	Chloroform	5.579	83	85		
31	Cyclohexane	5.668	84	69		
32	2,2-Dichloropropane	5.088	77	79	41	
33	1,2-Dichloroethane-d4- SURR	6.196	65	67	102	
34	Dibromofluoromethane- SURR	5.783	111	113	81	192
35	1,2-Dichloroethane	6.291	62	64	98	
36	1,1,1-Trichloroethane	5.710	97	99		
37	1,1-Dichloropropene	5.919	110	75	77	
38	Carbon Tetrachloride	5.856	117	119	82	
39	Benzene	6.155	78	77	79	
40	Dibromomethane	7.342	93	174	172	
41	1,2-Dichloropropane	7.211	63	41	76	
42	Trichloroethene	6.918	130	97	95	
43	Methyl Methacrylate	7.368	41	69	100	
44	Bromodichloromethane	7.520	83	85	127	
45	2-Nitropropane *** (or 46??)	7.854	41	39	46	
46	2-Chloroethyl Vinyl Ether	7.881	63	106	65	
47	cis-1,3-Dichloropropene	8.001	75	77	110	
48	4-Methyl-2-Pentanone (MIBK)	8.179	43	58	100	
49	Chlorobenzene-d5- ISTD	9.690	117	82	119	54
50	d8-Toluene- SURR	8.21	98	100	70	
51	trans-1,3-Dichloropropene	8.608	75	77		
52	Ethyl Methacrylate	8.66	69	41		
53	1,1,2-Trichloroethane	8.78	97	99	85	
54	Toluene	8.278	91	92		
55	1,3-Dichloropropane	8.947	76	78		
56	2-Hexanone	9.031	43	58	100	
57	Dibromochloromethane	9.131	129	127		
58	1,2-Dibromoethane (EDB)	9.246	107	109	188	
59	Tetrachloroethene	8.796	164	166	129	131
60	1,1,1,2-Tetrachloroethane	9.816	131	133	117	
61	Chlorobenzene	9.716	112	114	77	
62	Ethylbenzene	9.810	106	91		

63	m&p-Xylenes	9.936	106	91	105	
64	o-Xylene	10.328	106	91	105	
65	Styrene	10.360	104	103	78	
66	1,4-Dichlorobenzene-d4- ISTD	12.028	152	150	115	
67	1,1,2,2-Tetrachloroethane	11.071	83	85	131	
68	Bromoform	10.553	173	175	171	
69	1,2,3-Trichloropropane	11.118	110	75		
70	trans-1,4-Dichloro-2-butene	11.139	89	75	124	88
71	Isopropylbenzene (Cumene)	10.689	105	120		
72	Bromofluorobenzene- SURR	10.883	174	95	176	
73	Bromobenzene	11.013	77	156	158	
74	n-Propylbenzene	11.102	120	91		
75	2-Chlorotoluene	11.202	91	126	89	
76	4-Chlorotoluene	11.322	91	126	63	
77	1,3,5-Trimethylbenzene	11.291	105	120		
78	Pentachloroethane	11.646	117	167	165	83
79	1,2,4-Trimethylbenzene	11.662	105	91	77	51
80	tert-Butylbenzene	11.594	119	91	134	
81	sec-Butylbenzene	11.819	105	134		
82	1,3-Dichlorobenzene	11.955	146	148	111	
83	1,4-Dichlorobenzene	12.054	146	148		
84	p-Isopropyltoluene	11.971	119	91	134	
85	1,2-Dichlorobenzene	12.426	146	148	111	
86	n-Butylbenzene	12.378	91	92	134	
87	1,2-Dibromo-3-chloropropane (DBCP)	13.236	157	75	155	
88	1,2,4-Trichlorobenzene	14.026	180	182	145	
89	Naphthalene	14.277	128	127		
90	Hexachlorobutadiene	14.151	225	223	227	
91	1,2,3-Trichlorobenzene	14.523	180	182	145	
92	2-Methylnaphthalene	15.428	142	141	115	
Oxy	tert- Amyl methyl ether	6.394	73	55	87	
Oxy	tert- Butyl alcohol	3.660	59	41		
Oxy	Diisopropyl ether	4.476	45	87	59	
Oxy	Ethyl tert- butyl ether	4.988	59	57	87	
TBA	tert- Butyl acetate	7.116	57	43	59	101
DCFM	Dichlorofluoromethane	2.072	67	69	47	

MA	Methyl acetate	3.227	43	74	59	
MCH	Methyl cyclohexane	7.501	83	55	98	
THF	Tetrahydrofuran	5.466	42	71	72	

Title: SW-846 8270C - Base Neutral/Acid Organics by GC/MS

USEPA SW-846 3rd Edition, 8270C and 8000B

Approvals (Signature/Date):

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1.0 Scope and Application

1.1 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra.

1.2 Method 8270C, as directed in this SOP, is used to determine the concentration of semi-volatile organic compounds, in methylene chloride extracts prepared from various types of solid and liquid wastes, soils, and water samples.

1.3 Non-Aqueous Samples are prepared using Pressurized Fluid Extraction (3545)and/or Waste Dilution (3580A). Aqueous samples are prepared using Liquid-Liquid Continuous (3520), and/or Separatory Funnel (3510).

1.4 Method 8270 can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons (PAH's or PNA's), chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

- Additional compounds may be analyzed using this procedure, provided all appropriate quality control measures are evaluated and found acceptable. For OVAP, only compounds listed in the method may be reported using this procedure

1.5 On occasion clients may request slight modifications to this SOP. These modifications are handled as indicated in DT-QAM-001, Quality Assurance Manual.. **OVAP does not allow modifications to this SOP.**

1.6 The Method Reporting Limits (MRL) are approximately 75-330 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 5 to 10 µg/L for aqueous samples. Example Method Reporting Limits can be found in Table 1. Method Reporting Limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory-specific, method detection limit (MDL) data, project specific DQOs, regulatory requirements are all taken into account, as well as instrument-to-instrument repeatability.

2.0 Summary of Method

2.1 Samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation technique.

2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS), connected to the gas chromatograph.

2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authenticated standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve. Additional points may be analyzed, but the Method Reporting Limit must be supported by a low standard and a minimum of five points must be maintained.

3.0 Definitions

3.1 BNA - Base-neutral, acid extracted semi-volatiles, acronym for Method 8270

3.2 GC - Gas chromatograph

3.3 GC/MS - Gas Chromatograph Mass Spectrometer

3.4 EICP - Extracted Ion Current Profile, a plot of ion abundances versus time or scan number.

3.5 CCV - Continuing Calibration Verification .

3.6 SPCC - System performance check compounds.

3.7 CCC - Calibration Check compounds.

3.8 DFTPP - Decafluorotriphenylphosphine (DFTPP), tune check compound.

3.9 PAH - Polyaromatic hydrocarbons, also referred to as PNA

3.10 MRL- Method Reporting Limit

3.11 Please see the Glossary in the Quality Assurance Manual, DT-QAM-001 for additional definitions.

4.0 Interferences

4.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation or analysis of the samples and take corrective action to eliminate the problem.

4.2 Rinsing the syringes well, both the syringe used for sample prep and sample injection, prior to and after use, for each sample or standard is critical. Assigning separate functions to the syringes prevents cross-contamination (introduction of compounds from one sample to a sample not originally containing those compounds).

4.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent blank to check for cross-contamination.

4.4 The following compounds may require special treatment when being determined by this method:

4.4.1 Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.

4.4.2 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the GC, chemical reaction in acetone solution, and photochemical decomposition.

4.4.3 N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.

4.4.4 N-nitrosodiphenylamine decomposes in the GC inlet and cannot be separated from diphenylamine.

4.4.5 Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

4.4.6 Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), 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

5.1.1 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.2 The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.1.3 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

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 standards 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
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Sylon- CT 5% in Toluene	Flammable Carcinogen Teratogen Reproductive hazard Severe eye irritant Skin irritant	Toluene 200 ppm PEL 200 ppm TWA Ceiling 500 Maximum	May cause respiratory track irritation. Vapors may cause drowsiness or dizziness. Exposure to the eyes will cause sever irritation.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, and productivity or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Gas chromatograph/mass spectrometer system

- Agilent 5973
- Column - 50 m x 0.2 mm ID, 0.33 um film thickness, silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

6.2 Mass spectrometer - Capable of scanning from 35 to 500 amu, every 1 sec. or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 4 when 1 µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

6.3 Data system – A computer system is interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that

allows integrating the abundances in any EICP between specified time, or scan-number limits. A copy of the EPA/NIST or Wiley Mass Spectral Library must also be available.

6.4 Miscellaneous Items

- Autosampler syringes - 5 µL and 10 µL.
- Microsyringes for standards/sample preparation.
- Volumetric flasks, Class A - Appropriate sizes with ground-glass stoppers.
- Vials - Both pre-silanized and non-silanized glass, with polytetrafluoroethylene (PTFE)-lined screw caps or crimp caps.
- Analytical balance, capable of accuracy to 0.0001 g.
- Injection port liners. Single goose-neck recommended.
- Fused silica wool for injection port liners.
- Injection port septa, gold seals, liner o-rings various graphite-vespel ferrules.
- GC/MS filaments.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, or productivity. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

7.1 Stock standard solutions must be replaced after one year or sooner if comparison with quality control check samples indicate a problem. Store, protected from light, at <6.0°C. Stock standard solutions must be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration or evaporation, especially just prior to preparing calibration standards from them.

7.2 Organic-free reagent water.

7.3 Methanol, reagent grade.

7.4 Methylene chloride, pesticide quality or equivalent.

7.5 Stock Standard Solutions - Purchased as pre-mixed certified solutions. See Tables 2, 2a, 2b, 2c.

7.6 Premixed, certified internal standard solution containing d_4-1,4-dichlorobenzene, d_5-naphthalene, d_{10}-acenaphthene, d_{10}-phenanthrene, d_{12}-chrysene and d_{12}-perylene at 2000 ng/µL. Supelco.

7.7 Decafluorotriphenylphosphine (DFTPP), pentachlorophenol and benzidine. Supelco.

7.8 GC/MS tuning standard. See Table 3c.

7.9 Premixed, Certified Surrogate Spike Solution containing d6-phenol, 2-fluorophenol, 2,4,6-tribromophenol, d5-nitrobenzene, 2-fluorobiphenyl, and d14-p-terphenyl at 2,500 – 5,000 µg/mL. Supelco and Restek.

7.10 Sylon CT. Supelco.

7.11 Preparation of 8270 Standards - All standards are stored in amber, presilanized vials.

7.11.1 DFTPP Tune Check Standard (50 ng/ µL) –Transfer an aliquot of the prepared standard to an autosampler vial for analysis.

7.11.2 8270 Calibration Primary Dilution Standard (400 µg/mL). See Table 2

7.11.3 8270 LCS Primary Dilution Standard (200 µg/mL). See Table 2a.

7.11.4 8270 Appendix IX Primary Dilution Standard (400 µg/mL). See Table 2b.

7.11.5 8270 Calibration Standards. Prepare as indicated in Table 3. Standards are stored in presilanized crimp vials and can be re-used for several days if promptly re-capped and returned to the freezer. An expiration date is assigned for 6-months from date of preparation or less as indicated by the manufacturer.

7.11.6 8270 Appendix IX Calibration Standards. Prepare as indicated in Table 3a. Standards are stored in presilanized crimp vials and can be re-used for several days if promptly re-capped and returned to the freezer. An expiration date is assigned for 6-months from date of preparation or less as indicated by the manufacturer.

7.11.7 8270 CCV (50 µg/mL). Prepare as indicated in Table 3. An expiration date is assigned for 6-months from date of preparation or less as indicated by the manufacturer.

7.11.8 8270 Appendix IX CCV (50 µg/mL). Prepare as indicated in Table 3a. 6-months from date prepared or less as indicated by the manufacturer's expiration date.

7.11.9 8270 Appendix IX Extra CCV. Prepare as indicated in Table 3b. An expiration date is assigned for 6-months from date prepared or less as indicated by the manufacturer's expiration date.

7.11.10 8270 LCS/ICV (50 µg/mL). Add 250 µL of the 8270 LCS Primary Dilution Standard (200 µg/mL) to a 1mL volumetric. Add 10 µL of Restek Acid Surrogate Mix (10000 µg/mL) and 10 µL of Restek Base Surrogate Mix (5000 µg/mL). Bring to volume (1mL) with methylene chloride. Add 20 µL of internal standard and transfer solution to an autosampler vial to be injected onto the instrument. Prepare a LCS/MS/MSD spike by diluting 250 µL of 8270 LCS Primary Dilution Standard (200 µg /mL) in 750 µL of methanol. Mix well and add 1 mL of this solution to 1L of organic-free reagent water (LCS) or to two 1-L aliquots of samples (MS/MSD). An expiration date is assigned for 6-months from date of preparation or less as indicated by the manufacturer.

7.11.11 8270 Internal Standard (µg/mL). The sealed ampule that is provided by the manufacturer is opened and transferred to an amber, presilanized screw cap autosampler vial. No dilutions are necessary. An expiration date is assigned as 12 months or less as indicated by the manufacturer.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

OVAP and most other environmental samples require compliance with the information detailed in the analytical methods.

8.1 Listed below are the holding times and the references that include preservation requirements.

Matrix *	Sample Container *	Min. Sample Size	Preservation	Holding Time	Reference
Water	Amber Glass	1 L	Cool <6.0°C, but not frozen.	7 days from collection to extraction	SW-846 Chapter 4
Non-Aqueous	8oz glass	50g	Cool<6.0°C, but not frozen.	14 days from collection to extraction	SW-846 Chapter 4
Extracts	2mL amber autosampler vials	N/A	Protect from light.	40 days from extraction to analysis	SW-846 Chapter 4

8.2 *For concrete and other unusual matrices, the samples may be collected in plastic bottles, plastic bags or other containers.

9.0 Quality Control

9.1 Preparation QC

Quality Controls	Frequency	Comments
Method Blank (MB)	1 per preparation batch[1]	For soils, use sand or other clean solid matrix
Laboratory Control Sample (LCS)	1 per preparation batch[1]	For soils, use sand or other clean solid matrix
Matrix Spike/ Matrix Spike Duplicate (MS/MSD)[2]	1 per preparation batch[1]	If there is insufficient sample for an MS/MSD, note this on the bench-sheet, along with the reason
Surrogates	Each standard and sample	

[1]Preparation batch is limited to 20 samples

[2]The sample selection for MS/MSD is random, unless specifically requested by a client

9.2 Analytical QC

Quality Controls	Frequency	Comments
Tune check (DFTPP)	1 per 12 hr clock	Initiates the 12 hr clock.
Calibration Verification Standard	1 per 12 hr clock	New Initial Calibration must be performed if CCV fails and corrective action does not result in an acceptable CCV
Initial Calibration	As needed	Minimum of 5 calibration points
Internal Standards	Each standard and sample	

9.3 **Method Blank** - A method blank must be included with every extraction batch but not necessarily every instrument run batch.

9.3.1 Typically, the method blank is analyzed prior to sample analysis to insure the chromatographic system is contaminant-free.

9.3.2 When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the method blank associated with those samples (e.g., extracted with the samples) must be analyzed on at least one of those instruments.

9.3.3 Acceptance criteria is <MRL. If the method blank shows a detection above the required Method Reporting Limit, it must be reanalyzed. If this fails to correct the problem, all associated samples with concentrations above the Method Reporting Limit, for that analyte, must be re-extracted.

9.3.4 If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag detections for the failing analyte in the affected samples, LCS, MS/MSD with a "B". For OVAP, provide an explanation in the QC narrative.

- If the associated samples are non-detect, then reanalysis of the Method Blank is not required and re-extraction of samples is not required.
- If the concentration found in the samples is >10X the concentration found in the Method Blank, reanalysis is not required, but data must be flagged. **This exception is not allowed by OVAP.**

9.3.5 The laboratory must not subtract results of the method blank from those of any associated samples. Such "blank subtraction" is inappropriate.

9.3.6 Method blanks may be used to check contamination by carryover from a high-concentration sample into subsequent samples. If the analytes in the high-concentration sample are not present in the subsequent blank, then lack of carryover has been demonstrated.

9.4 **Laboratory Control Sample (LCS)** - must be included with every extraction batch but not necessarily with every analytical run batch.

9.4.1 Typically, the LCS is analyzed prior to samples to verify acceptable batch control before proceeding with sample analysis.

9.4.2 When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the LCS associated with those samples (e.g., extracted with the samples) must be analyzed on at least one of those instruments.

9.4.3 The LCS may be spiked with and/or evaluated for a limited list of target analytes, provided this is acceptable to the regulatory program for which samples are being analyzed.

9.4.4 Control limits are maintained in LIMS. If the LCS fails to meet criteria, then the extraction batch is considered out-of-control for the compounds that failed and re-extraction/re-analysis for those compounds must be performed before results are reported.

9.4.5 If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag detections for the failing analyte in the affected samples, LCS and Method Blanks, do not flag the MS/MSD. For OVAP, provide an explanation in the QC narrative.

- If the LCS recovery is high, associated samples that are <MRL are not required to be re-extracted, but must be flagged.

9.5 **Surrogates** - All samples and standards are spiked with three acid-extractable surrogates and three base-neutral-extractable surrogates.

9.5.1 If only acids are being analyzed, then it is acceptable to spike with only the acid surrogates, if only base-neutrals are being analyzed, then it is acceptable to spike with only the base-neutral surrogates. In either case, it is acceptable to spike with all six surrogates.

9.5.2 Established limits are maintained in the LIMS.

9.5.3 Any sample, including batch QC, with surrogates outside the control limits requires evaluation by the laboratory. Once the problem has been identified and addressed, corrective action may include the reanalysis of samples, or the extraction and analysis of new sample aliquots.

9.5.4 If the samples are for OVAP Program, then any sample extract, including Method Blank and or/LCS, with a surrogate outside the acceptance limits must be reanalyzed and/or re-extracted if a matrix effect cannot be demonstrated.

- If the individual sample surrogate recoveries are high, and the associated analytes are non-detect, then reanalysis and/or re-extraction is not necessary.
- If the Method Blank or LCS has high surrogate recovery, and the samples are non-detect for the associated analytes, then reanalysis of the batch is not necessary.
- If there is an obvious matrix effect as evidenced by chromatography, or other physical matrix issue, re-extraction is not required. Flag surrogate recovery in the individually affected samples, MS/MSD. For OVAP, provide an explanation in the QC narrative.
- If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag surrogate recovery in the individually affected samples, Method Blank, LCS, MS/MSD. For OVAP, provide an explanation in the QC narrative.

9.6 **Matrix Spike/Matrix Spike Duplicate (MS/MSD) -** One sample in every 20 samples should be prepared in triplicate and two replicates must be spiked with the LCS standard described above. These replicates are known as the matrix spike (MS) and matrix spike duplicate (MSD)

9.6.1 The MS/MSD may be spiked with and/or evaluated for a limited list of target analytes, provided this is acceptable to the regulatory program for which samples are being analyzed

9.6.2 The MS/MSD criteria is maintained in LIMS. See Section 11 for percent recovery and RPD calculations.

9.6.3 If the MS/MSD is outside of the limits flag the affected analyte in the parent sample, MS & MSD.

9.6.4 MS/MSD is not used to determine batch control.

9.6.5 If insufficient sample has been provided for a MS/MSD then make a note in the appropriate raw data or logbook.

9.7 **DFTPP Tune Check**. Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 50 ng or less injection. Typically a 1 µL injection of the DFTPP standard is injected. Analyses must not begin until these criteria are met. Injection of the DFTPP

initiates the 12-hour clock. All samples analyzed must be injected within 12 hours of the DFTPP injection.

9.7.1 Use the DFTPP mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g. CLP, Method 525 or manufacturer's instructions) provided the method performance is not adversely affected. All subsequent standards, samples, MS/MSDs, LCSs, and Method Blanks associated with a DFTPP analysis must use identical mass spectrometer instrument conditions. As 8270C specifically allows the use of other tuning criteria, all criteria listed as options are 8270C compliant.

9.7.2 The mass spectrum of DFTPP may be acquired in the following manner. Tune evaluations usually utilize the "Autofind" function and are set up to look at the apex +/- 1 scan and average the three scans. Background correction is required prior to the start of the peak but no more than 20 scans before. Background correction must not include any part of the target peak.

9.7.3 Other Options or if Autofind Fails

- "Autofind" is not an option for all versions of software, or sometimes the instrument does not always correctly identify the apex when the peak is not perfectly shaped. In this case, manually identify and average the apex peak +/- 1 scan and background correct as in 9.7.2 above.
- Or the scan across the peak at one half peak height may be averaged and background corrected.
- A single scan at the Apex (only) may also be used for the evaluation of the tune, background correction is still required.
- Changes such as adjustments to the repeller and ion focus lenses, adjusting the EM Voltage, etc. may be made prior to tune verification as long as all of the subsequent injections in the 12 hour tune cycle are analyzed under the same MS tune settings and it is documented in the run sequence log and/or maintenance log that an adjustment was made. Excessive adjusting (more than 2 tries) without clear documentation is not allowed. Necessary maintenance is performed and documented in instrument log.
- If source cleaning or other maintenance is performed then follow steps for tune evaluation above. The maintenance must be documented in the maintenance log and should be noted in the sequence run log. Note: If significant maintenance is performed, see methods 8000B or 8000C, then the instrument may require recalibration prior to proceeding.

9.7.4 Tune evaluation printouts should include the chromatogram and spectra as well as the Tune evaluation information.

9.7.5 Since the limits are expressed in whole percentages, the results may be rounded to whole percentage before comparing to criteria when assessing the tune verification against the tune requirements. However, the comparison to the criteria is usually done automatically by the software and if the printout says "Fail" then there would have to be documentation of the hand calculation on the raw data and comparison to the criteria if the lab intends to still accept the tune.

9.7.6 The instrument tune parameters are contained in a file that is referenced by the analytical method. To avoid the chance of error, it is recommended that the tune file be overwritten rather than renamed when an instrument tune is performed, so that editing the reference in the analytical method is not necessary.

9.7.7 All MS tune settings must remain constant between running the tune check and all other samples. It is recommended that a separate tune method not be used, however a separate method may be used as long as the MS conditions between the methods are the same so any changes that are made to the Mass Spec of Tune specifications in the analysis method are also made to the tune method.

9.7.8 These criteria must be demonstrated each 12-hour shift during which samples are analyzed. Injection of the DFTPP initiates the 12-hour batch. All subsequent samples in this 12-hour batch or work shift must be injected within 12 hours of the injection of DFTPP.

9.7.9 Any sample analyzed following a DFTPP that failed the above criteria must be re-analyzed. If no sample is available for re-analysis, data must be flagged and the client notified of the deviation.

9.7.10 The GC/MS tuning standard must also be used to assess GC column performance and injection port inertness. Benzidine and pentachlorophenol must be present at their normal responses (for 50 ng or less), and no peak tailing should be visible.

9.8 **Internal Standards** -All samples and standards are spiked with internal standards. Internal Standards are associated with specific analytes based on retention time. Only those internal standards associated with the target analytes need to be evaluated.

9.8.1 Sample internal standard responses acceptance criteria is –50% to +100% of the response in the CCV for that 12 hour shift. Samples with failing internal standards must be evaluated to determine if re-analysis and/or dilution must be performed to correct the deviations.

9.8.2 For OVAP, samples must not be reported with failing internal standards. If a matrix effect is confirmed, the sample must be diluted to bring the internal standard recoveries into limits.

- If there is potential for the direct analysis of the extract to cause harm to the analytical system, such as very dark or thick extracts, or suspected high levels of analyte or non-target analytes, then initial analysis of the extract may be performed at a dilution.
- If the initial diluted analysis yields a chromatogram that is clean, then samples must be reanalyzed less diluted, if possible.

9.8.3 If there are not obvious interferences, one sample from each affected project is reprocessed and reanalyzed to confirm a possible matrix effect. Reanalysis is performed at the original dilution (or undiluted), unless the extract is dark or thick, or otherwise expected to cause problems with the analytical system. If the recoveries confirm or there is obvious interference, results are reported from the original analysis and a qualifier is added. If the internal standard recoveries from the reprocessed sample fulfill criteria, all affected samples are reprocessed and results from the re-analyses are reported. The goal being to report samples with passing internal standards from the least diluted run. For OVAP samples, see section 9.8.2.

9.9 **Calibration range exceedence**. If any response exceeds the upper limit of the calibration, dilution of the sample is required to achieve a response that is within the calibration range.

- **Carryover**. Any detection of a compound following a sample with a high-concentration detection for the same compound should be considered suspect of

system carryover. Reanalysis is required to demonstrate carryover. The system should be considered contaminated until demonstrated otherwise via analysis of clean blanks or samples that show no contamination.

9.10 For Ohio VAP: The laboratory must implement corrective action procedures to resolve the deviation and limit qualification of the final results. The laboratory is not permitted to deviate from its VAP approved SOP if it intends to attest under affidavit that the "results" are VAP certified. When all corrective actions listed in the SOP have been exhausted, it may be necessary to use technical judgment in which case the decision process and rationale will be presented in the final report and/or affidavit **and the data will be noted as 'not VAP certified' on the affidavit.**

10.0 Procedure

10.1 Instrument Operating Conditions:

10.1.1 Recommended GC/MS Operating Conditions. See Table 6.

10.1.2 Routine daily maintenance is recommended. The maintenance may include replacement of the injection port liner and septa as well as trimming of the front end of the analytical column. Periodically, it may be necessary to replace the gold seal in the injection port.

10.1.3 Silanization of the injection port liner before installation is recommended. Add a small fused silica wool plug to a single gooseneck liner. Heat the liner in Sylon CT at 100 ^{o}C for 15 minutes. Cool, rinse 3-4 times with methanol and dry with a nitrogen stream.

10.1.4 Generally, expect to trim several centimeters off the column daily. It may be necessary to trim 1 meter or more following analyses of samples with high levels of contaminants. The column may need to be replaced if trimming does not eliminate active sites. Backup columns should be available for every instrument.

10.1.5 The GC/MS Ion Source will need to be cleaned on a frequent basis. It is recommended that several sets of spare filaments be available at all times.

10.2 **Initial calibration**. (periodic) Initial calibration standards must be prepared at a minimum of five different concentrations from the secondary dilution of stock standards. Prepare these solutions in methylene chloride. At least one of the calibration standards must correspond to a concentration at or below the desired Method Reporting Limit. Typically, this method is calibrated at 2.5-120 µg/L for aqueous samples and 75-3600 µg/Kg for soils.

10.2.1 Prepare and analyze a tune check as in section 9.7.

10.2.2 The internal standards selected should permit most of the components of interest in a chromatogram to have retention times of 0.80 – 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation. If interferences are noted, use the next most intense ion as the quantitation ion.

10.2.3 Analyze each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte. Calculate response factors (RF) for each target analyte as described in Section 11. A system performance check should be made before this calibration curve is used.

10.2.3.1 SPCCs - Check the SPCC compounds to determine if the calculated average RF has met the minimum response factor criteria outlined in

Table 5.

Four compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum response factor of 0.050

- These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

  N-nitroso-di-n-propylamine

  Hexachlorocyclopentadiene

  2,4-dinitrophenol

  4-nitrophenol

- If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

10.2.3.2 CCCs - Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration. See Section 11 for calculations. Typically the RSD will be less than or equal to 15% for each target analyte. However the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%.

- See Table 5 for the CCC compounds.
- If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Perform maintenance - which may include cleaning or replacing the injector liner and/or capillary column, then repeat the calibration procedure.
- If the CCCs are not included in the list of analytes for a project then all target compounds for that project must meet the same criteria as the CCCs or an RSD of less than or equal to 30%.

10.2.4 Linearity. Assess the linearity of the calibration.

- If the %RSD of the response factor is <15%, linearity through the origin can be assumed and the average response factor can be used in place of a calibration curve for quantitation.
- If the %RSD is > 15%, linearity through the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that is not forced through zero. This approach may also be employed based on past experience or priori knowledge of the instrument response. This is most easily achieved by performing a linear regression of the instrument response versus concentration of the standards. See Section 11 for linear regression calculations. The calibration is considered to be acceptable if the linear

regression correlation coefficient, r, is greater than or equal to 0.99. (Enviroquant calculates r^2, which must be greater than or equal to 0.980.)

- A quadratic or second order model may also be employed but at least six points must be used. In order to be used for quantitative purposes, r must be greater than or equal to 0.99. Enviroquant calculates r^2 which must be greater than or equal to 0.980. **These curve fits can only be used for compounds that historically exhibit a non-linear response and can not be used to extend the calibration range for those compounds that normally exhibit a linear response but within a narrower calibration range.**
- If the calibration fails to meet the linearity criteria, corrective action must be taken which may include instrument maintenance, reanalysis of a single standard or reanalysis of the entire calibration curve.

10.2.5 Retention Time - The relative retention time of each target analyte in each calibration standard should agree within 0.06 relative retention time units. The internal standards selected for each compound should permit relative retention times of 0.8-1.20.

10.2.6 Any sample analyzed following a calibration curve that does not meet the criteria addressed above must be re-analyzed with a valid calibration.

10.2.7 If no sample is available for re-analysis, re-analysis is not required. Flag detections for the failing analyte in the affected samples.

10.2.8 Selecting Calibration Points - Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed then the Method Reporting Limit is raised to be equivalent to the lowest level used in the calibration curve. In any event the number of levels remaining in the calibration must be at least that required by the method.

10.2.8.1 Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method.

10.2.8.2 Removal of points from the middle of a calibration curve, or replacement of any points in the curve is not permitted unless an injection, instrument, or other physical cause can be confirmed, see below. Supervisor approval and sign-off is required.

10.2.8.3 One of the following conditions must be satisfied to allow for removal or replacement of a level:

- The data file is corrupted and unusable or the run is interrupted before completion.
- The analyst observes and documents a problem such as leaking of a purge vessel.
- For internal standard methods, the recovery of the internal standards is less than 70% or greater than 130% of the recovery in the other standards, or the amount of analyte recovered is less than 70% or greater than 130% of the expected values (indicating an improperly made up standard).
- For external standard methods, the unit response of the analyte is less than 70% or greater than 130% of the average unit response

for the analyte in the other calibration standards (indicating an improperly prepared standard or bad injection).

10.2.8.4 The injection, instrument or other physical cause must be limited to those points in question and must be clearly documented on the runlog and/or raw data.

10.2.8.5 If reanalysis and replacement is being done, it should be done as soon as possible, but must be done prior to the injection/analysis of any samples.

NOTE: Removal of points for individual analytes from levels other than the highest and lowest is not permitted in any event.

10.2.9 In some instances, it may not be practical to analyze a calibration curve in one 12-hour batch. Analysis of calibration standards may continue in a second batch provided no samples have been analyzed.

10.3 Initial Calibration Verification (ICV) – The analysis of an independent reference standard or ICV is required following each curve. This standard is prepared at a mid-level calibration level, typically 50 µg/mL as described above. The acceptance limits for all target analytes and surrogates are ±30%.

10.3.1 If the ICV analyte (or surrogate) has a response that exceeds the recovery criteria, and the associated samples are non-detect for that analyte, then the sample data may be used without qualification and reanalysis is not required.

10.3.2 Certain appendix IX compounds are very reactive and do not perform well. They are considered acceptable in the ICV if the recovery is ±60%.

- Isosafrol
- Diallate
- methapyriliene

10.4 Continuing Calibration Verification (CCV)- Daily The initial calibration curve for each compound of interest must be verified once every 12 hours prior to sample analysis. This is accomplished by analyzing a mid-point standard, typically 50 µg/L, that contains all target compounds of interest. The results from the calibration standard analysis must meet the verification acceptance criteria provided in Table 5 before any samples can be analyzed.

10.4.1 SPCCs - The minimum response factors criteria of 0.05 must be met for the SPCCs (See Table 5). If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins.

- Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, active sites in the column or chromatographic system.

10.4.2 CCCs - After the system performance check is met, the CCCs listed in Table 5 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor calibration and percent drift when calibrating using a regression fit model. Refer to Section 11 for percent difference and percent drift calculations. If the percent drift or percent difference for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If

the criteria is not met (i.e. greater than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the problem cannot be corrected by other measures, a new initial calibration must be generated and the CCC criteria met before sample analysis begins.

- If the CCCs are not included in the list of analytes for a project, and therefore are not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

10.4.3 Non CCC target analytes have an acceptance criteria of 40% difference or drift with the exception of poor performers which have an acceptance criteria of 50% . Poor performers are:

- Benzoic acid
- Benzidine
- 3,3'-Dichlorobenzidine
- 4,6-dinitro-2-methylphenol
- 2,4-dinitrophenol
- 4-nitrophenol
- Hexachlorocyclopentadiene
- N-nitrosodi-n-propylamine

10.4.4 <u>Internal standards</u>

- Response – If the EICP area for any of the internal standards in the CCV change 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.
- Retention time –Retention times are affected by oven temperatures, column flow, length of column and other factors. The nature of this analysis is such that trimming length from the column is done on a routine basis to eliminate interferences and contaminants that may result from injection of samples. This trimming results in a shorter column, therefore affecting retention time. The retention times of the internal standards in the CCV must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes unexpectedly by more than 30 seconds from that in the most recent CCV, 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.

10.4.5 Surrogate acceptance criteria in the CCV are ±30%.

10.4.6 Evaluating the CCV for a short target list: If the CCCs are not included in the list of analytes for a project, and therefore are not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

- Problems with CCVs may be due to standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, active sites/leaks in the column or purge and trap system or other analytical system issues. Problems may also be due to simple error in preparation of the standard.

10.4.7 Any sample analyzed after a CCV that failed any of the criteria above must be re-analyzed. If no sample is available for re-analysis, data must be flagged and the client notified of the deviation.

10.4.8 If the CCV analyte has a response that exceeds the recovery criteria, and the associated samples are non-detect for that analyte, then the sample data may be used without qualification and reanalysis is not required.

10.5 Sample Analysis:

10.5.1 DFTPP tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

10.5.2 Prior to analysis, each sample extract must be spiked with internal standard. 20 µL of the internal standard mix described above (2000 µg/mL) is added to each 1 mL sample extract (10 µL to 0.5 mL extract). If a different amount of extract is used, the amount of internal standard used must be adjusted accordingly.

10.5.3 Inject an aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration. The volume injected is typically 2 µLs. The volume injected must be the same for all samples as was used in the calibration.

10.5.4 If the response for any target quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (40 ng/ µL).

10.6 Qualitative Analysis:

The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions in a reference mass spectrum are defined to be 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. Compounds are identified as present when the following criteria are met.

10.6.1 The intensities of the characteristic ions (see Tables 7 and 7a) of a compound maximize in the same scan or within one scan or each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

10.6.2 The relative retention time (RRT) of the sample component is within ±0.06 RRT units of the RRT of the standard component.

10.6.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

10.6.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

10.6.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

10.6.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

10.6.7 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

10.6.8 For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Please note: OVAP does not certify for Tentative Identified Compounds- as such any TICs must be excluded from the OVAP affidavit. Use the following guidelines for making tentative identifications:

- Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

10.7 <u>Quantitative Analysis:</u>

10.7.1 Once a compound is identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

10.7.2 If the RSD of a compound's response factors is <15%, then the concentration in the extract may be determined using the average response factor from the initial calibration data. See Section 11 for calculation details.

10.7.3 If the RSD is >15%, then an appropriate curve fit is applied and used to determine the concentration in extract.

10.7.4 Where applicable, the concentration of any non-target analytes (TICS, Tentatively Identified Compounds) identified in the sample may be estimated. The sample formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

10.7.5 Where TICs are reported, the resulting concentration should be reported indicating that the value is an estimate. Use the nearest internal standard free of interferences.

11.0 Calculations/ Data Reduction

11.1 Response factors (RF)

$$RF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:

A_x = Area of characteristic ion for compound being measured.
C_{is} = Concentration of the specific internal standard.
A_{is} = Area of characteristic ion for the initial standard.
C_x = Concentration of the compound being measured.

11.2 Standard Deviation

SD = Standard Deviation of initial 5 RFs for each compound calculated as follows:

$$SD = \sqrt{\sum_{i=1}^{n} \frac{\left(x_i - \overline{x_i}\right)^2}{n-1}}$$

$\overline{x_i}$ = Mean (Average) of initial 5 RFs for each compound.

n = number of standards

x_i = individual RF

11.3 Relative Standard Deviation (%RSD)

$$\%RSD = \frac{SD}{RF_{ave}} \times 100$$

where:

RF_{ave} = The average of the 5 or more initial calibration RFs
SD = The standard deviation of the average RFs

11.4 **Linear Regression Calculation**

This calculation is used when the %RSD exceeds 20%.

$$y = ax + b$$

where:

y = Instrument response (total area sum)
a = Slope of the line (coefficient of x)
x = Concentration of calibration standard
b = The intercept

The Enviroquant data system is capable of generating a linear plot. The analyst should **not** force the line through the origin.

11.5 The mathematics used in least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves generated tend to fit points at the upper calibration levels better than points at the lower calibration levels. To compensate for this, a weighting factor which reduces this tendency is used. Examples of acceptable weighting factors which place more emphasis on numbers of smaller value are:

$w = 1/y$ or $w = 1/y^2$

11.6 **Coefficient of Determination**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2}$$

Correlation Coefficient

$$r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response
x = Concentration

11.7 <u>Percent Difference</u> (%D)

$$\%D = \frac{[RF_{ave} - RF_c]}{[RF_{ave}]} \times 100$$

where:

RF_{ave} = The average of the 5 or more initial calibration RFs
RF_c = Continuing calibration RF

11.8 % Drift Calculation

% Drift calculation in used for comparing continuing calibration responses to a **linear** curve. The criteria for % Drift is the same as for % Difference.

$$\%\text{Drift} = \frac{\text{Calculated concentration - Theoretical concentration}}{\text{Theoretical concentration}} \times 100\%$$

11.9 Extract (raw) concentration- using average curve fit

$$Conc_{RAW} = (At / Ais)Conc_{IS}$$

Where:
A_T = Area of sample peak
A_{IS} = Area of internal standard
$Conc_{IS}$ = Concentration of Internal standard

11.10 Extract (raw) concentration- using linear regression

$$Conc_{RAW} = \left(\frac{\left(\frac{A_T}{A_{IS}} - b \right)}{a} \right) Conc_{IS}$$

Where:
A_T = Area of sample peak
A_{IS} = Area of internal standard
b = The intercept
a = Slope of the line (coefficient of x)
$Conc_{IS}$ = Concentration of Internal standard

11.11 Extract (raw) concentration- using quadratic fit

$R = aConc^2 + bConc + c$

Where Conc = Concentration of analyte in extract

$$ConcRAW = \left[\frac{-b \pm \sqrt{b^2 - 4a\left[c - \left(\frac{A_T}{A_{IS}}\right)\right]}}{2a} \right] Conc_{IS}$$

Where:
A_T = Area of sample peak
A_{IS} = Area of internal standard
b = constant
a = constant
c = constant
Conc $_{IS}$ = Concentration of Internal standard

11.12 Concentration of Semi-Volatiles in Aqueous samples

$$\textbf{Conc. (µg/Kg)} = \frac{(C_r)(Vf)(DF)}{(W_s)(Vi)}$$

Where: C_r = Concentration reported by the data system in µg/mL.
Vi = Initial Volume of sample extracted
Vf = Final Volume of extract
DF = Dilution factor

11.13 Concentration of Semi-Volatiles in Soil/Sediment samples

$$\textbf{Conc. (µg/Kg)} = \frac{(C_r)(DF)}{(W_s)(S)}$$

Where: C_r = Concentration reported by the data system in µg/mL.
W_s = Wet Weight of sample extracted, grams
S = Solid fraction, % solids/100 , optional
DF = Dilution factor

11.14 Surrogate % Recovery

$$\textbf{\% Recovery} = \frac{\textbf{Concentration detected}}{\textbf{Concentration spiked}} \times 100$$

11.15 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Percent Recovery or LCS Percent Recovery:

$$\textbf{\%Recovery} = \frac{(S-U)}{T} \times 100$$

Where: S = Spiked result
U = Unspiked result (use 0 for LCS)
T = Spike True Concentration

This formula is used to calculate LCS recoveries as well. C_x = 0 in the LCS.

11.16 Relative Percent Difference (RPD) of Matrix Spikes

$$\textbf{RPD} = \frac{\textbf{(Larger value - Smaller Value)}}{\textbf{(Average of the Values)}} \times 100$$

12.0 Method Performance

12.1 The supervisor has responsibility to ensure that an analyst who has been performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Method Detection Limit Study – A method detection limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Demonstration of Capabilities - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.2 The following waste streams are produced when this method is carried out:

- Autosampler vials containing Methylene Chloride are collected in 55 gallon drums and disposed of through a Waste Handler.
- Waste Methylene Chloride rinses are collected, drummed, and disposed of through a Waste Handler.

15.0 References/ Cross References

15.1 SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", 3rd Edition, Methods referenced are Method 8000B, 8270C.

15.2 SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", 2ndEdition, Methods referenced is Method 8270C

15.3 **This is an OVAP approved SOP. All changes, other than formatting or spelling, made to this SOP must be approved by OVAP prior to implementation.**

15.4 DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton

15.5 DT-QA-005 Procedure for Balance Calibration Check

15.6 DT-QA-006 Thermometer Calibration

15.7 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.

16.0 Method Modifications

None

17.0 Attachments

Table 1. Example Method Reporting Limits
Table 2. Preparation of 8270 Primary Dilution Standard
Table 2a. Preparation of 8270 LCS Primary Dilution Standard
Table 2b. Preparation of 8270 Appendix IX Primary Dilution Standard
Table 2c. 8270 Appendix IX Extra Source Standards
Table 3. 8270 Calibration Standard Preparation
Table 3a. 8270 Appendix IX Calibration Standard Preparation
Table 3b. 8270 Apppendix IX Extra Calibration Standard Preparation
Table 3c. 8270 Tune Check Standard Preparation
Table 4. DFTPP Key Ions & Ion Abundance Criteria
Table 5. 8270 SPCC & CCC Calibration & CCV Criteria
Table 6. Recommended GC/MS Operating Conditions
Table 7. Characteristic Ions for 8270 Compounds
Table 7a. Characteristic Ions for 8270 Appendix IX Compounds

18.0 Revision History

18.1 Revision Dates

- 7/21/11 Biannual review
- 8/24/07

18.2 Changes from last revision

Item	Change from	Change to	Reason
Copyright	2007 information	2011 information	Policy is updated annually to reflect new year.
1.1	Added	This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra.	Consistency with other SOPs
4.4	Added	Additional compounds may be analyzed using this procedure, provided all appropriate quality control measures are evaluated and found acceptable. For OVAP, only compounds listed in the method may be reported using this procedure	Consistency with other SOPs
All SOP	Reporting Limit	Method Reporting Limit	Consistency in terminology with other SOPs

Item	Change from	Change to	Reason
6.3	The most recent version of the EPA/NIST or Wiley Mass Spectral Library should also be available.	A copy of the EPA/NIST or Wiley Mass Spectral Library must also be available.	Actual lab procedure
8	Paragraph format	Table format	Consistency with other SOPs
8	Added	OVAP and most other environmental samples require compliance with the information detailed in the analytical methods.	OVAP SOP contents
8.2	Added	*For concrete and other unusual matrices, the samples may be collected in plastic bottles, plastic bags or other containers.	OVAP SOP contents
9	Paragraph format	Table format	Consistency with other SOPs
9.4.3	Added	The LCS may be spiked with and/or evaluated for a limited list of target analytes, provided this is acceptable to the regulatory program for which samples are being analyzed.	Clarify procedure
9	Added	Corrective action for failed QC parameters	OVAP SOP contents
9.10	Added	See text in body of SOP	OVAP SOP contents
10	Added	Corrective action for failed calibration criteria	OVAP SOP contents
15	Added	• DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton • DT-QA-005 Procedure for Balance Calibration Check • DT-QA-006 Thermometer Calibration • DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.	Ancillary SOPs

Table 1. Example Method Reporting Limits

Analyte	soil ug/Kg	water ug/L
1,2,4-Trichlorobenzene	147	5
1,2-Dichlorobenzene	147	5
1,2-Dinitrobenzene	147	5
1,3-Dichlorobenzene	147	5
1,3-Dinitrobenzene	147	5
1,4-Dichlorobenzene	147	5
1,4-dinitrobenzene	147	5
1-Methylnaphthalene	147	5
2,2-oxybis(1-Chloropropane)	147	5
2,3,4,6-Tetrachlorophenol	294	10
2,3,5,6-Tetrachlorophenol	294	10
2,3-Dichloroaniline	147	5
2,4,5-Trichlorophenol	294	10
2,4,6-Trichlorophenol	294	10
2,4-Dichlorophenol	294	10
2,4-Dimethylphenol	294	10
2,4-Dinitrophenol	588	20
2,4-Dinitrotoluene	147	5
2,6-Dichlorophenol	294	10
2,6-Dinitrotoluene	147	5
2-Chloronaphthalene	147	5
2-Chlorophenol	294	10
2-Methylnaphthalene	147	5
2-Methylphenol	294	10
2-Nitroaniline	294	10
2-Nitrophenol	294	10
3&4-Methylphenol	294	10
3,3-Dichlorobenzidine	1471	50
3-Nitroaniline	294	10
4,6-Dinitro-2-methylphenol	294	10
4-Bromophenyl-phenylether	147	5
4-Chloro-3-methylphenol	294	10
4-Chloroaniline	147	5
4-Chlorophenyl-phenylether	147	5
4-Nitroaniline	294	10
4-Nitrophenol	294	10
Acenaphthene	147	5
Acenaphthylene	147	5
Acetophenone	147	5
Aniline	294	10
Anthracene	147	5
Benzidine	1471	50
Benzo(a)anthracene	147	5

Benzo(a)pyrene	147	5
Benzo(b)fluoranthene	147	5
Benzo(g,h,i)perylene	147	5
Benzo(k)fluoranthene	147	5
Benzoic acid	1471	50
Benzyl Alcohol	294	10
bis(2-Chloroethoxy)methane	147	5
bis(2-Chloroethyl)ether	147	5
bis(2-Ethylhexyl)adipate	147	5
bis(2-Ethylhexyl)phthalate	147	5
Butylbenzylphthalate	147	5
Carbazole	147	5
Chrysene	147	5
Dibenz(a,h)anthracene	147	5
Dibenzofuran	147	5
Diethylphthalate	147	5
Dimethylphthalate	147	5
Di-n-butylphthalate	147	5
Di-n-octylphthalate	147	5
Diphenylhydrazine(Azobenzene)	147	5
Fluoranthene	147	5
Fluorene	147	5
Hexachlorobenzene	147	5
Hexachlorobutadiene	147	5
Hexachlorocyclopentadiene	588	20
Hexachloroethane	147	5
Indeno(1,2,3-c,d)pyrene	147	5
Isophorone	147	5
Naphthalene	147	5
n-decane	147	5
Nitrobenzene	147	5
N-Nitrosodimethylamine	147	5
N-Nitrosodi-n-propylamine	147	5
N-Nitrosodiphenylamine as DPA	147	5
n-Octadecane	147	5
Pentachlorophenol	294	10
Phenanthrene	147	5
Phenol	294	10
Pyrene	147	5
Pyridine	147	5

NOTE: Sample MRLs are highly matrix-dependent. The MRLs listed herein are provided for guidance and may not always be achievable.

Table 2. Preparation of 8270 Primary Dilution Standard

Vendor	Product #	Name	Conc. (µg/mL)	Volume (mLs)
8270 Mega Primary Dilution Standard:				
Supelco	5-06508	CLP Semivolatiles Calibration Mix	1000	2
Ultra	CUS-8375	Custom Standard	2000	1
Supelco	86-8055	NET BNA Surrogate Std.	5000/2500	0.8
Fisher		Methylene Chloride		1.2
8270 Benzidine Primary Dilution Standard:				
Supelco	4-8906	TCL Benzidines Mix	2000	1
Fisher		Methylene Chloride		4

NOTE: If different source concentrations are purchased, the preparation volumes will have to be modified.

Table 2a. Preparation of 8270 LCS Primary Dilution Standard

Vendor	Product #	Name	Conc. (µg /mL)	Volume (mLs)
Restek	31850	8270 MegaMix	1000	2
Restek	561053	Custom SV Standard	2000	1
Restek	31030	605 Benzidines Cal Mix	2000	1
Fisher		Methylene Chloride	2000	6

Table 2b. 8270 Appendix IX Primary Dilution Standard (Custom Standards)- Source used for prep in 3a

Vendor		Product #	Conc. (µg /mL)	Volume (mLs)
Supelco		20005868	2000	1 mL
Supelco		20005875	2000	1 mL
Supelco		20005880	2000	1 mL
Supelco		20005882	2000	1 mL
Supelco		20005885	2000	1 mL

Table 2c. 8270 Appendix IX Extra Source Standards (used in prep for 3b)

Vendor	Product #	Name	Conc. (µg /mL)
Supelco	47519-U	Aramite	2000
Supelco	4-0323	Hexachlorophene	5000
Accustandard	P-147S-10X	Famphur	1000
Accustandard	P-152S-10X	Kepone	1000

Table 3. 8270 Calibration Standard Preparation

Calibration Level (ppm)	Volume of Mega Primary Std. (µLs)	Volume of Benzidine Primary Std. (µLs)	Volume MeCl2 (µLs)	Volume Internal Std. (µLs)
2.5	6.25	6.25	987.5	20
5	12.5	12.5	975	20
10 *	25	25	950	20
20	25	25	450	10
50 (CCV)	125	125	750	20
80	100	100	300	10
100	125	125	250	10
120	150	150	200	10

* Accustandard APP-9-086-20X (2000 µg /mL)

Table 3a. 8270 Appendix IX Calibration Standard Preparation

Calibration Level (ppm)	Volume of App. IX Primary Std. (µLs)	*Volume of a,a-Dimethylphenethyl -amine (µLs)	Volume MeCl2 (µLs)	Volume Internal Standard (µLs)
20	50	10	940	20
30	75	15	910	20
40	50	10	440	10
50 (CCV)	125	25	850	20
60	75	15	410	10
80	100	20	380	10
100	125	25	350	10
120	150	30	320	10

* Accustandard APP-9-086-20X (2000 µg /mL)

Table 3b. 8270 Appendix IX Extra Calibration Standard Preparation

Calibration Level	Volume Aramite, µL	Volume Famphur µL	Volume Hexachlorophene µL	Volume Kepone µL	Volume Internal Standard µL	Volume MeCl2 µL
20	10	20	16	40	20	914
40	20	40	32	80	20	828
50 (CCV)	25	50	40	100	20	785
60	30	60	48	120	20	742
80	40	80	64	160	20	656
100	50	100	80	200	20	570

Table 3c. 8270 Tune Check Standard Preparation

	Std. Volume (µL)	Final Conc. in Standard (ppm)	Final Volume
Restek Tune Mix with DDT 1000µg/mL	500		10mL
Methylene Chloride	9500	n/a	
DFTPP		50	
Pentachlorophenol		50	
Benzidine		50	
DDT		50	

Table 4 DFTPP Key Ions and Ion Abundance Criteria

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 to 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

Table 5. 8270 SPCC and CCC Calibration and CCV Criteria.

SPCCs:	
Compound	**Minimum RF**
2,4-Dinitrophenol	0.05
4-Nitrophenol	0.05
Hexachlorocyclopentadiene	0.05
N-Nitroso-di-n-propylamine	0.05

CCCs:		
Compound	**Maximum RSD**	**Maximum % Drift**
Acid Fraction:		
4-Chloro-3-methylphenol	30%	20%
2,4-Dichlorophenol	30%	20%
2-Nitrophenol	30%	20%
Phenol	30%	20%
Pentachlorophenol	30%	20%
2,4,6-Trichlorophenol	30%	20%
Base/Neutral Fraction:		
Acenaphthene	30%	20%
1,4-Dichlorobenzene	30%	20%
Hexachlorobutadiene	30%	20%
Diphenylamine	30%	20%
Di-n-octyl phthalate	30%	20%
Fluoranthene	30%	20%
Benzo(a)pyrene	30%	20%

Table 6. Recommended GC/MS Operating Conditions:

Inlet Mode	Split
Split ratio	10:1
Total flow	25 ml/min
Injector temperature	250 ^{o}C
Head Pressure	60 psi (for a 50 M column)
Injection volume	2 µL (using a 5 µL syringe)
Detector B (GC/MS Interface) Temperature	280 ^{o}C
Column:	Varian VF5-ms 50M x0.20mm x 0.33 um
Oven Program:	
Initial Temperature	70 ^{o}C
Initial Time	3.75 min
Ramp 1 Program Rate	35 ^{o}C/min
Ramp1 Final Temperature	190 ^{o}C
Ramp 1 Final Time	0 min
Ramp 2 Program Rate	30 ^{o}C/min
Ramp 2 Final Temperature	295 ^{o}C
Ramp 2 Final Time	0 min
Ramp 3 Program Rate	25 ^{o}C/min
Ramp 3 Final Temperature	345 ^{o}C
Ramp 3 Final Time	Until Benzo(ghi)perylene elutes
MS Threshold	150
Mass range	34-550
Scan time	To give at least 3 scans/peak
Sample #	2
A/D Samples	4
GCMS 5973 only:	
MS Quad	150 ^{o}C
MS Source	230 ^{o}C

Table 7. Characteristic Ions for 8270 compounds

COMPOUND	RT	QUANT IONS	SECONDARY IONS		
d4-1,4-Dichlorobenzene (IS)	6.17	152	150	115	
N-Nitrosodimethylamine	2.56	74	42	43	
Pyridine	2.64	79	52	51	
2-Fluorophenol	4.56	112	64	92	
d6-Phenol	5.74	99	71		
Phenol	5.75	94	66	65	
Aniline	5.82	93	66	65	
bis(2-Chloroethyl)ether	5.87	93	95		
n-Decane	5.94	57	43	142	
2-Chlorophenol	5.94	128	130	129	
1,3-Dichlorobenzene	6.11	146	148	111	
1,4-Dichlorobenzene	6.18	146	148	111	
1,2-Dichlorobenzene	6.34	146	148	111	
Benzyl Alcohol	6.30	79	108	50	
2-Methylphenol	6.40	108	107	90	79
3&4-Methylphenol	6.55	107	108	77	
2,2'-oxybis(1-Chloropropane)	6.41	45	121	77	
Acetophenone	6.56	105	77	120	
N-Nitrosodi-n-propylamine	6.56	70	101	130	43
Hexachloroethane	6.67	119	117	121	
d5-Nitrobenzene	6.72	82	128	54	
Nitrobenzene	6.74	77	123	51	65
d8-Naphthalene (IS)	7.36	136	137		
Isophorone	6.94	82	138		
2-Nitrophenol	7.03	139	81	39	
2,4-Dimethylphenol	7.03	107	122	121	
bis(2-Chloroethoxy)methane	7.11	93	123	95	63
Benzoic acid	7.13	105	77	122	
2,4-Dichlorphenol	7.23	162	164	63	
2,6-Dichlorphenol	7.42	162	164	63	
1,2,4-Trichlorobenzene	7.30	180	182	184	
Naphthalene	7.38	128	129		
4-Chloroaniline	7.41	127	129	65	
Hexachlorobutadiene	7.46	225	227	223	
4-Chloro-3-methylphenol	7.79	107	142	144	
2-Methylnaphthalene	7.94	142	141	115	
1-Methylnaphthalene	8.03	142	141	115	
Hexachlorocylcopentadiene	8.06	237	235	239	
d10-Acenaphthene (IS)	8.80	164	162	160	
2,4,6-Trichlorphenol	8.17	196	200	198	
2,4,5-Trichlorphenol	8.20	196	198	200	
2,3-dichloroaniline	8.18	165	89	63	

Table 7. Characteristic Ions for 8270 compounds

COMPOUND	RT	QUANT IONS	SECONDARY IONS		
2-Fluorobiphenyl	8.22	172	171	170	
2-Chloronaphthalene	8.35	162	164	127	
2-Nitroaniline	8.43	65	138	92	
3-Nitroaniline	8.76	65	138	92	
4-Nitroaniline	9.26	138	65	92	
1,4-dinitrobenzene	8.52	168	122	92	
1,3-dinitrobenzene	8.59	168	122	92	
1,2-dinitrobenzene	8.66	168	122	92	
Dimethylphthalate	8.53	163	194	164	
2,6-Dinitrotoluene	8.60	165	89	63	
2,4-Dinitrotoluene	8.93	165	89	63	
Acenaphthylene	8.69	152	151	153	
2,4-Dinitrophenol	8.83	184	107		
Acenaphthene	8.83	153	154	152	
4-Nitrophenol	8.85	65	109	139	
Dibenzofuran	8.96	168	139		
2,3,5,6-tetrachlorophenol	9.02	232	230	234	131
2,3,4,6-tetrachlorophenol	9.05	232	230	234	131
Diethylphthalate	9.07	149	150	177	
4-Chlorophenyl-phenylether	9.20	204	206	141	
Fluorene	9.25	166	165	167	
4,6-Dinitro-2-methylphenol	9.26	198	105	121	
N-Nitrosodiphenylamine as DPA	9.30	169	168	167	
Diphenylhydrazine (Azobenzene)	9.34	77	51	105	182
d10-Phenanthrene (IS)	10.02	188	189		
2,4,6-Tribromophenol	9.45	330	332	328	
4-Bromophenyl-phenylether	9.61	248	250	141	
Hexachlorobenzene	9.70	284	286	282	
n-Octadecane	9.76	57	71	254	
Pentachlorophenol	9.85	266	268	264	
Phenanthrene	10.05	178	176	179	
Anthracene	10.09	178	176	179	
Carbazole	10.20	167	166	139	140
Di-n-butylphthalate	10.38	149	150		
Fluoranthene	11.04	202	200	203	
Benzidine	11.12	184	185		
d12-Chrysene (IS)	12.30	240	241		
Pyrene	11.25	202	200	203	
d14-p-Terphenyl	11.31	244	245	122	
bis(2-Ethylhexyl)adipate	11.65	129	147	112	
Butylbenzylphthalate	11.67	149	150	206	
bis(2-Ethylhexyl)phthalate	12.11	149	167		
3,3'-Dichlorobenzidine	12.22	252	254		

Table 7. Characteristic Ions for 8270 compounds

COMPOUND	RT	QUANT IONS	SECONDARY IONS		
Benzo(a)anthracene	12.29	228	229	114	
Chrysene	12.32	228	229	114	
Di-n-octylphthalate	12.67	149	150		
d12-Perylene (IS)	13.66	264	265		
Benzo(b)fluoranthene	13.26	252	250	253	
Benzo(k)fluoranthene	13.29	252	253	250	
Benzo(a)pyrene	13.61	252	253	250	
Dibenz(a,h)anthracene	14.89	278	279		
Indeno(1,2,3-c,d)pyrene	14.91	276	274		
Benzo(g,h,I)perylene	15.30	276	274	277	

Table 7a. Characteristic Ions for 8270 Appendix IX Compounds

COMPOUND	RT	QUANT ION	SECONDARY IONS		
d4-1,4-Dichlorobenzene (IS)	9.42	152	150	115	
3-Methylphenol	10.25	107	108	79	
Methyl Methanesulfonate	6.70	80	79	65	
2-Picoline	5.66	93	66	78	
N-Nitrosodiethylamine	7.48	42	102	57	
Ethyl Methanesulfonate	8.05	79	109	97	
N-Nitrosomethylethylamine	5.99	42	88	43	
Pyridine	3.67	79	52	51	
Ethylmethacrylate	4.75	69	41		
Penachloroethane	8.89	117	119	167	
d8-Naphthalene (IS)	12.01	136	137		
2,6-Dichlorphenol	12.21	162	164	63	98
N-Nitrosopyrrolidine	10.19	41	100	42	
4-Nitrosomorpholine	56.00	116	86		
a,a-Dimethylphenethylamine	11.73	58	91		
Acetophenone	10.22	105	77	120	
Hexachloropropene	12.25	213	215	211	
Safrole	13.43	162	77	131	
o,o,o-Triethylphosphorothioate	11.47	198	126		
o-Toluidine	10.29	106	107		
N-Nitrosodi-n-butylamine	12.97	84	57	41	
N-Nitrosopiperidine	10.87	42	55	114	
d10-Acenaphthene (IS)	16.02	164	162	160	
p-Phenylenediamine	12.97	108	80	107	
2-Naphthylamine	16.70	143	115	116	
1-Naphthylamine	16.90	143	115	116	
1,3-Dinitrobenzene	15.49	50	76	75	168
1,2,4,5-Tetrachlorobenzene	13.99	216	214	218	

Table 7a. Characteristic Ions for 8270 Appendix IX Compounds

COMPOUND	RT	QUANT ION	SECONDARY IONS		
1,4-Naphthoquinone	15.14	158	76	102	104
2,3,4,6-Tetrachlorphenol	16.81	232	230	234	
Isosafrole	14.62	162	131	104	
Thionazin	17.33	97	96	107	
d10-Phenanthrene (IS)	19.35	188	189		
4-Aminobiphenyl	17.66	169	168	167	
5-Nitro-o-toluidine	17.38	152	77	106	
Phenacetin	18.44	108	109	179	
Diallate	18.35	86	234	43	
Aramite	25.31	185	135	319	
Chlorobenzilate	22.15	139	251	253	
Penachloronitrobenzene	19.02	237	214	295	
Methapyrilene	20.85	58	97		
4-Nitroquinoline-1-oxide	20.71	190	89	160	
Dimethoate	18.72	87	93	125	
Disulfoton	19.4	88	97	89	
Parathion	20.69	97	109	291	
1,3,5-Trinitrobenzene	18.32	213	75	120	63
Methyl Parathion	20.05	109	125	263	
Pentachlorobenzene	16.41	250	252	248	
Sulfotepp	18.1	97	322	202	
Phorate	18.37	75	97	121	
Pronamide	19.18	173	175	145	
Dinoseb	19.38	211	163	240	
Isodrin	21.1	193	195	263	66
d12-Chrysene (IS)	23.3	240	241		
2-Acetylaminofluorene	22.88	181	223	152	
Kepone	28.29	272	274	270	237
Hexachlorphene	30.15	196	198	406	408
Famphur	27.31	218	125	93	
p-(Dimethylamino)-azobenzene	22.08	120	225	77	
3,3'-Dimethylbenzidine	22.53	212	213		
d12-Perylene (IS)	25.01	264	265		
7,12-Dimethylbenz(a)anthracene	24.57	256	241	239	
3-Methylcholanthrene	25.31	268	252	253	

Title: Pesticides

USEPA SW-846 Method 8081, Revision 1, December 1996.

Approvals (Signature/Date):

7/22/11	7/22/11
Josh McKinney Department Manager	Date	Jason Lykins EH&S Officer	Date
7/22/11	7/22/11
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1.0 Scope and Application

1.1 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.2 Method 8081 is used to determine the concentrations of various organochlorine pesticides in extracts from solid and liquid matrices, using fused silica, open-tubular, capillary columns with electron capture detectors (ECD). When compared to the packed columns, these columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis.

- Additional compounds may be analyzed using this procedure, provided all appropriate quality control measures are evaluated and found acceptable. For OVAP, only compounds listed in the method may be reported using this procedure

1.3 Non-Aqueous Samples are prepared using Pressurized Fluid Extraction (3545), Ultrasonic Extraction (3550) and/or Waste Dilution (3580A). Aqueous samples are prepared using Liquid-Liquid Continuous (3520), and/or Separatory Funnel (3510).

1.4 A variety of cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes. Suggested cleanups include alumina (Method 3610), Florisil (Method 3620), silica gel (Method 3630), gel permeation chromatography (Method 3640), and sulfur (Method 3660).

1.5 The analyst must select columns, detectors and calibration procedures most appropriate for the specific analytes of interest in a study. Matrix-specific performance data must be established and the stability of the analytical system and instrument calibration must be established for each analytical matrix (e.g., hexane solutions from sample extracts, diluted oil samples, etc.).

1.6 Although performance data are presented for many of the target analytes, it is unlikely that all of them could be determined in a single analysis. The chemical and chromatographic behaviors of many of these chemicals can result in co-elution of some target analytes. Several cleanup/fractionation schemes are provided in this method and in Method 3600.

1.7 Several multi-component mixtures (i.e., Chlordane and Toxaphene) are listed as target analytes. When samples contain more than one multi-component analyte, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of multi-component analytes that have been subjected to environmental degradation or degradation by treatment technologies. These result in “weathered” multi-component mixtures that may have significant differences in peak patterns than those of standards.

1.8 Compound identification based on single-column analysis must be confirmed on a second column, or must be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurements made with the primary column. GC/MS Method 8270 is also recommended as a confirmation technique, if sensitivity permits.

1.9 This method includes a dual-column option. The option allows a hardware configuration of two analytical columns joined to a single injection port. The option allows one injection to be used for dual-column analysis. Analysts are cautioned that the dual-column option may not be appropriate when the instrument is subject to mechanical stress, many samples are to be run in a short period, or when contaminated samples are analyzed.

1.10 The Method Reporting Limits (MRL) are approximately 50 µg/kg (wet weight) for

soil/sediment samples and 0.1 µg/L for aqueous samples. Example Method Reporting Limits can be found in Table 8. Method Reporting Limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory-specific, method detection limit (MDL) data, project specific DQOs, regulatory requirements are all taken into account, as well as instrument-to-instrument repeatability.

1.11 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis As indicated in the QAManual. **OVAP does not allow modifications to this SOP.**

2.0 Summary of Method

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 10 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 After clean-up, the extract is analyzed by injecting a sample into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector.

3.0 Definitions

3.1 DCB - Surrogate Decachlorobiphenyl.

3.2 TCX - Surrogate Tetrachloro-m-xylene

3.3 Primary and Secondary Column – The primary column refers to the column which is normally used for quantitation. The secondary column is normally used for qualification only. Either column can be used for quantitation and reporting if it meets the acceptance criteria.

3.4 Please see the Glossary in the Quality Assurance Manual, DT-QAM-001 for additional definitions.

4.0 Interferences

4.1 Sources of interference in this method can be grouped into three broad categories.

4.1.1 Contaminated solvents, reagents, or sample processing hardware.

4.1.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

4.1.3 Compounds extracted from the sample matrix to which the detector will respond.

4.1.4 Interferences co-extracted from the samples vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

4.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. This interference can best be minimized by avoiding contact with plastic materials and checking all solvents and reagents for phthalate contamination. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

4.3 Glassware must be scrupulously cleaned. Extraction glassware is detergent washed with hot water and rinsed with tap water and organic-free reagent water. This is followed by methylene chloride and methanol rinses.

4.4 The presence of elemental sulfur will result in broad peaks that interfere with the detection

of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. Method 3660 is suggested for removal of sulfur. The TBA procedure is not used because the recovery of Endrin aldehyde is drastically reduced.

4.5 Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. Method 3630 (silica gel), Method 3620 (fluorisil), or Method 3610 (alumina) are recommended for elimination of the co-elutors. PCBs may interfere with the analysis of pesticides, particularly the multicomponent analytes such as Chlordane or Toxaphene.

4.6 Co-elution among the many target analytes in this method can cause interference problems.

4.7 Poor GC performance may be expected when a chromatographic system is contaminated with high-boiling point materials, particularly in the injector. Routine maintenance must be performed such as replacement of septa, metal seals, liners and removing as much as 0.5 – 1 M from the injector side of the capillary column.

4.8 Carrier gas should be scrubbed to remove traces of oxygen and scrubbers should be changed regularly. Carrier gas should always be passed through the column whenever the oven is heated.

4.9 GC injector ports can be of critical concern, especially in the analysis of DDT and Endrin. Injectors that are contaminated, chemically active, or too hot can cause the degradation ("breakdown") of the analytes. Endrin and DDT breakdown to Endrin aldehyde, Endrin ketone, DDD and DDE.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), 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

5.1.1 Latex and vinyl gloves provide no protection against the organic solvents used in this method. Nitrile or similar gloves must be used.

5.1.2 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.3 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

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 standards 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
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sylon-CT (5% in Toluene)	Flammable Carcinogen Teratogen Reproductive hazard Severe eye irritant Skin irritant	Toluene 200 ppm PEL 200 ppm TWA Ceiling 500 Maximum	May cause respiratory track irritation. Vapors may cause drowsiness or dizziness. Exposure to the eyes will cause sever irritation.
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

The following items are recommended for performing this procedure. Equivalent items should only be used or when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Gas chromatograph: an analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, autosamplers, electron capture detectors (ECD), and data system. It is recommended that the system be equipped with two ECDs The Agilent Technologies Model 5890 or 6890 is preferred.

6.2 The data acquisition system must be capable of time stamping all data produced with the correct date and time. If regression is to be used in place of average response factor calibration, the system must be capable of plotting the curves and calculating correlation coefficients.

6.3 GC columns. The following pairs of columns are used:

- Restek Rtx-CLPesticides 30m, 0.32mm ID, 0.50um (Cat. #11139)
- Restek Rtx-CLPesticides2 30m, 0.32mm ID, 0.25um (Cat. #11324)

6.4 5 µL or 10 µL autosampler syringes.

6.5 Restek Siltek single gooseneck injection port liners.

6.6 Restek Ice Blue Injection port septa.

6.7 Restek Siltek injection port seals.

6.8 Class A Volumetric flasks of varying concentrations for preparation of standards.

6.9 Microsyringes of varying volumes for preparation of standards and dilution of samples.

6.10 Amber 2 mL crimp top vials with crimp caps.

6.11 Reagent bottles for standards storage. Caps must be Teflon-lined.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

7.1 All standards are stored at <-10.0°C unless otherwise recommended by the manufacturer. Reagents are stored at room temperature, unless otherwise recommended by the manufacturer.

7.2 All stock standard solutions must be replaced after one year or sooner if routine QC tests indicate a problem. All other standard solutions must be replaced after six months or sooner if routine QC indicates a problem.

7.3 Organic-free reagent water.

7.4 n-Hexane, pesticide grade or better.

7.5 Acetone, pesticide grade or better.

7.6 Methylene chloride, pesticide grade or better.

7.7 Methanol, reagent grade or pesticide grade.

7.8 Calibration standards and verification standards. See Tables 2 & 3 for preparation details.

7.9 Supelco Sylon CT 5% for silanization of standards glassware.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

8.2 OVAP and most other environmental samples require compliance with the information detailed in the analytical methods.

8.3 Listed below are the holding times and the references that include preservation requirements.

Matrix *	Sample Container *	Min. Sample Size	Preservation	Holding Time	Reference
Aqueous	1L (or 1gal) amber glass with Teflon-lined lids	1L	Cool <6.0°C, but not frozen	7 days from collection to extraction	SW-846 Chapter 4
Non-aqueous	Glass with Teflon-lined lids.	20 g	Cool <6.0°C, but not frozen	14 days from collection to extraction	SW-846 Chapter 4
Extracts	n/a	n/a	Cool <6.0°C, but not frozen, store in dark	40 days from extraction to analysis	SW-846 Chapter 4

8.4 * For concrete and other unusual matrices, the samples may be collected in plastic bottles, plastic bags or other containers.

8.5 All samples and/or sample extracts are stored separately from standards.

9.0 Quality Control

9.1 Preparation QC

Quality Controls	Frequency	Acceptance Limits
Method Blank (MB)	1 per preparation batch[1]	<MRL.
Laboratory Control Sample (LCS)	1 per preparation batch[1]	Historic limits are maintained in LIMSs
Matrix Spike (MS)[2]	1 per preparation batch[1]	Historic limits are maintained in LIMSs
Matrix Spike Duplicate (MSD)[2]	1 per preparation batch[1]	Historic limits are maintained in LIMSs
Surrogates	Each standard and sample	Historic limits are maintained in LIMSs

[1]A preparation batch is limited to 20 samples.
[2]The MS/MSD are randomly selected, unless specifically requested by a client.

9.2 Analytical QC

Quality Controls	Frequency	Comments
Initial Calibration	As needed	Minimum of 5 calibration points
Continuing Calibration Verification	1 per 12 hr clock	New Initial Calibration must be performed if CCV fails and corrective action does not result in an acceptable CCV
Endrin/DDT Breakdown	1 per 12 hr clock	Required for all analyses, even short lists that do not include Endrin or DDT as targets

9.3 **Method Blank** - A Method Blank must be included with every extraction batch but not necessarily every instrument run batch.

9.3.1 Typically, the Method Blank is analyzed prior to sample analysis to insure the chromatographic system is contaminant-free.

9.3.2 When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the Method Blank associated with those samples (e.g., extracted with the samples) must be analyzed on at least one of those instruments.

9.3.3 Acceptance criteria is <MRL. If the Method Blank shows a detection above the required Method Reporting Limit, it must be reanalyzed. If this fails to correct the problem, all associated samples with concentrations above the Method Reporting Limit, for that analyte, must be re-extracted.

9.3.4 If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag detections for the failing analyte in the affected samples, LCS, MS/MSD with a "B". For OVAP, provide an explanation in the QC narrative.

- If the associated samples are non-detect, then reanalysis of the Method Blank is not required and re-extraction of samples is not required.
- If the concentration found in the samples is >10X the concentration found in the Method Blank, reanalysis is not required, but data must be flagged. **This exception is not allowed by OVAP.**

9.3.5 The laboratory must not subtract results of the Method Blank from those of any associated samples. Such "blank subtraction" is inappropriate.

9.3.6 Method Blanks may be used to check contamination by carryover from a high-concentration sample into subsequent samples. If the analytes in the high-concentration sample are not present in the subsequent blank, then lack of carryover has been demonstrated.

9.4 **Laboratory Control Standard (LCS)** - An LCS is extracted with every extraction batch.

9.4.1 Typically, the LCS is analyzed prior to samples to verify acceptable batch control before proceeding with sample analysis.

9.4.2 When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the LCS associated with those samples (e.g., extracted with the samples) must be analyzed on at least one of those instruments.

9.4.3 The LCS may be spiked with and/or evaluated for a limited list of target analytes, provided this is acceptable to the regulatory program for which samples are being analyzed.

9.4.4 Control limits are maintained in LIMS. If the LCS fails to meet criteria, then the extraction batch is considered out-of-control for the compounds that failed and **re-extraction/re-analysis for those compounds must be performed before results are reported.**

9.4.5 If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag detections for the failing analyte in the affected samples, LCS and Method Blanks, do not flag the MS/MSD. For OVAP, provide an explanation in the QC narrative.

- If the LCS recovery is high, associated samples that are <MRL are not required to be re-extracted, but must be flagged.

9.5 **Surrogates** - All samples and standards are spiked with surrogates. Two surrogates are spiked, and TCX is used as the primary surrogate for Pesticides

9.5.1 Established limits are maintained in the LIMS.

9.5.2 Any sample, including batch QC, with surrogates outside the control limits requires evaluation by the laboratory. Once the problem has been identified and addressed, corrective action may include the reanalysis of samples, or the extraction and analysis of new sample aliquots.

9.5.3 If the samples are for OVAP Program, then any sample extract, including Method Blank and or/LCS, with a surrogate outside the acceptance limits must reanalyzed and/or re-extracted if a matrix effect cannot be demonstrated.

- If the individual sample surrogate recoveries are high, and the associated analytes are non-detect, then reanalysis and/or re-extraction is not necessary.
- If the Method Blank or LCS has high surrogate recovery, and the samples are non-detect for the associated analytes, then reanalysis of the batch is not necessary.
- If there is an obvious matrix effect as evidenced by chromatography, sample foaming, or other physical matrix issue, re-extraction is not required. Flag surrogate recovery in the individually affected samples, MS/MSD. For OVAP, provide an explanation in the QC narrative.
- If there is insufficient sample or if re-extraction will result in missed hold times, re-extraction of samples is not required. Flag surrogate recovery in the individually affected samples, Method Blank, LCS, MS/MSD. For OVAP, provide an explanation in the QC narrative.

9.6 **Matrix Spike/Matrix Spike Duplicate (MS/MSD)** - When adequate sample is provided, one sample in each batch is spiked with the LCS spike described above to demonstrate any matrix interferences.

9.6.1 The MS/MSD may be evaluated for a limited list of target analytes, provided this is acceptable to the regulatory program for which samples are being analyzed

9.6.2 The MS/MSD criteria is maintained in LIMS. See Section 11 for percent recovery and RPD calculations.

9.6.3 If MS/MSD recovery or RPD is out of limits Flag the affected analyte in the parent sample, MS & MSD.

9.6.4 The MS/MSD is not used for batch control.

9.6.5 If there is insufficient sample or an MS/MSD is not performed for other reasons, make a note in the appropriate raw data or logbook.

9.7 For Ohio VAP: The laboratory must implement corrective action procedures to resolve the deviation and limit qualification of the final results. The laboratory is not permitted to deviate from its VAP approved SOP if it intends to attest under affidavit that the "results" are VAP certified. When all corrective actions listed in the SOP have been exhausted, it may be necessary to use technical judgment in which case the decision process and rationale will be presented in the final report and/or affidavit **and the data will be noted as 'not VAP certified' on the affidavit.**

10.0 Procedure

10.1 **Extract cleanup** - Cleanup procedures may not be necessary for a relatively clean sample matrix, but some extracts from environmental and waste samples require additional preparation before analysis. The specific cleanup procedure used depends on the nature of the sample to be analyzed and the data quality objectives for the measurements.

10.1.1 Method 3610 (alumina) may be used to remove phthalate esters.

10.1.2 Method 3620 (fluorisil) may be used to separate organochlorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds.

10.1.3 Method 3630 (silica gel) may be used to separate single component organochlorine pesticides from some interferents.

10.1.4 Elemental sulfur, which may be present in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in Method 3660.

10.2 **Instrument Operating Conditions**

10.2.1 Single-column analysis with the use of two narrow bore capillary columns each attached to separate injector systems

10.2.2 Table 7 lists typical GC operating conditions.

10.2.3 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a week or more. Therefore the GC column should be primed (or deactivated) by injecting a pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

10.3 **Endrin/DDT Breakdown -**The breakdown of DDT and Endrin must be measured before samples are analyzed and at the beginning of each 12-hour shift.

10.3.1 Acceptance criteria is <15% for either compound.

10.3.2 Corrective action may include Injector cleaning or silanization, installing a new injection port liner, new septa and/or a new inlet seal. Trimming the column at least 30 cm at the injector side may also be helpful.

10.3.3 No samples can be analyzed until the Endrin/DDT breakdown is <15%. Any sample analysis associated with an Endrin/DDT check with >15% breakdown must be re-analyzed with breakdown in control.

10.4 **12-Hour Run Batch** - is initiated with the successful analysis of the Endrin/DDT. The batch may include as many injections as can be made within 12 hours of the injection of the Endrin/DDT check,up to a maximum of 20 client samples. The batch must be concluded with a post-run CCV. Any sample analyzed outside the 12-hour clock must be re-analyzed.

10.5 **Initial Calibration** (periodic)

10.5.1 Prepare a minimum of five single component pesticide calibration standards as described in Table 2. There must be a point in the curve at, or below, the Method Reporting Limit. Store the standards in reagent bottles that have been silanized with Sylon CT.

10.5.2 Analyze the calibration standards.. Calculate the Response Factor (RF) for each analyte at each concentration, the mean Response Factor and the relative standard deviation (RSD) of the Response Factors. If the RSD for each analyte is less than or equal to 20%, then the response of the instrument is considered linear and the mean or average Response Factor can be used to quantitate sample results.

10.5.3 If the RSD is >20%, then linearity through the origin cannot be assumed and the

analyst must select a calibration curve or regression model. The regression calculation will generate a correlation coefficient (*r*) that is a measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, *r* must be greater than or equal to 0.99. (Enviroquant calculates r^2, r^2 must be greater than 0.980.)

10.5.4 If the initial calibration curve fails to meet the 20% RSD criterion or the *r*>0.99 regression criterion, the calibration is unsuccessful. Perform corrective action and recalibrate. Suggested corrective actions include injector/column maintenance, preparation of new calibration standards, installation of new columns, and/or refurbishment of the ECD detectors. If the calibration appears to fail for one standard only, that standard can be re-injected and the calibration criteria re-calculated as long as no samples have been analyzed.

- Samples must not be analyzed unless a valid initial calibration is first obtained

NOTE: **Pesticides as analyzed by this procedure exhibit a linear response. As such, Quadratic fits have been determined to be inappropriate for this analysis.**

10.5.5 Each initial calibration must be followed by a mid-range level standard of Chlordane and Toxaphene if these analytes are being tested. This is for pattern recognition only. If a sample has a pattern match for either analyte the sample must be rerun after a 5 point calibration for that analyte.

10.6 **Selecting Calibration Points** - Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed then the Method Reporting Limit is raised to be equivalent to the lowest level used in the calibration curve. In any event the number of levels remaining in the calibration must be at least that required by the method.

10.6.1 Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method.

10.6.2 Removal of points from the middle of a calibration curve, or replacement of any points in the curve is not permitted unless an injection, instrument, or other physical cause can be confirmed, see below.

10.6.3 One of the following conditions must be satisfied to allow for removal or replacement of a level:

- The data file is corrupted and unusable or the run is interrupted before completion.
- The analyst observes and documents a problem such as Z'd syringe
- For external standard methods, the unit response of the analyte is less than 70% or greater than 130% of the average unit response for the analyte in the other calibration standards (indicating an improperly prepared standard or bad injection).
- The injection, instrument or other physical cause must be limited to those points in question and must be clearly documented on the runlog and/or raw data.
- If reanalysis and replacement is being done, it should be done as soon as possible, but must be done prior to the injection/analysis of any samples.

NOTE: Removal of points for individual analytes from levels other than the highest and lowest is not permitted in any event.

10.6.4 In some instances, it may not be practical to analyze a calibration curve in one 12-hour batch. Analysis of calibration standards may continue in a second batch provided no samples have been analyzed.

10.7 **Initial Calibration Verification Standard (ICV)** - A standard from a source independent of the calibration standards is analyzed following every initial calibration curve. The quantitated results of the ICV must be within ± 30% of the true concentration of each analyte in the ICV.

10.7.1 If the ICV result is unacceptable, it may be reprepped and/or reanalyzed (provided no samples have been analyzed in the instrument). If this fails to correct the problem them perform other corrective action and reanalyze the initial calibration.

10.7.2 If the ICV recovery is high and associated samples are <MRL, then results may be reported without qualification.

10.8 **Continuing Calibration Verification (CCV)- Daily**

10.8.1 Endrin/DDT breakdown check must meet the criteria described in Section 10.3. The injection of this standard initiates the 12-hour batch or shift.

10.8.2 Continuing Calibration Verification (CCV) – Verify the calibration each 12-hour shift by injecting a CCV prior to conducting any sample analyses. A CCV must be injected at intervals of not less than once every 20 client samples and at the end of the analysis sequence. Note that injection of Method Blanks, LCSs, MS/MSDs or solvent blanks are not included in the 20 sample count.

10.8.3 When using an average curve fit, evaluate % difference from the mean Response Factor calculated for the initial calibration. When using regression, evaluate the % Drift. Acceptance criteria is±15% of the true value. See Section 11 for the calculations.

10.8.4 All samples must be bracketed with CCVs that meet this acceptance criteria for analytes of interest.

10.8.5 When a CCV fails to meet the QC criteria, all samples that were injected after the last CCV that passed must be re-injected.

- However, if the CCV exhibits a response for an analyte that is <u>above</u> the acceptance limit (>115%) and the analyte was <u>not</u> detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed and may be reported with qualifiers.

10.8.6 The first CCV of the run is also used to establish each analyte and surrogate retention time for the12-hour shift. (Daily maintenance of the GC may include removing a portion of the column. This action may result in a shift of retention times). However, if any subsequent CCV in the analytical sequence has an analyte which does not fall within its determined retention time window, the run is out of control and corrective action must be performed.

10.9 **Sample Analysis**

10.9.1 Samples and Extraction batch QC may be analyzed following successful calibration (periodic or daily). Generally it is advisable to analyze the extraction Method Blank and LCS prior to sample analysis.

10.9.2 Determine the concentration of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. Proper quantitation requires the appropriate selection of a baseline from which the peak area or height can be determined. Calculate concentration for all samples and extraction QC.

10.9.3 If the responses exceed the calibrated range of the system, dilute the extract and re-analyze.

10.9.4 Identification of mixtures (Chlordane or Toxaphene) is based on the characteristic "fingerprint" retention time and shape of the indicator peaks. Quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peaks of the same retention time and shape generated using the external calibration procedure.

10.9.5 Qualitative Identification - Second column confirmation is required to make a positive Identification for all single and multi-components pesticides.

- If there is a tentative hit in the RT Window for an analyte on the primary column, run a single point standard on a secondary column, at or below the Method Reporting Limit.
- Run the sample in question.
- Compare the RT of the analyte in question to that of the peak in the sample.
- If the peak in the sample is within the established RT window for the analyte, the ID is confirmed. The sample must be rerun against a valid 2nd column calibration to obtain quantitative identification. (see section 10.9.6)
- If the peak in the sample is not within the established RT window for the analyte, the ID is not confirmed and the sample is reported as ND for that analyte.
- Confirmation may not be necessary if composition of the sample matrix is well established by prior analysis or by process knowledge for instance, when a pesticide known to be produced or used in a facility is tested.

10.9.6 Quantitative Identification - Second column confirmation is required to assess quantitative comparison between columns, when single or multi-component pesticides show hits within the established RT Windows on both columns.

- When used to assess quantitative confirmation the second column must meet the same initial calibration and daily verification criteria as the primary column.
- When the sample results are confirmed using two dissimilar columns, the agreement between the quantitative results must be evaluated after the identification has been confirmed.
- Calculate the relative percent difference (RPD) as described in Section 11. If one result is significantly higher (e.g. >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or operator) during peak integration.
- If no chromatographic interference is noted, report the higher value unless - unless otherwise specified in an approved project plan. Qualify the data to indicate the disparity in the results.

- Confirmation may not be necessary if the composition of the sample matrix is well established by prior analysis or by process knowledge, for instance, when a pesticide known to be produced or used in a facility is tested.

11.0 Calculations / Data Reduction

Pesticides as analyzed by this procedure exhibit a linear response. As such, Quadratic fits have been determined to be inappropriate for this analysis.

11.1 Accuracy

$$\frac{\text{Concentration detected}}{\text{Concentration spiked}} \times 100$$

11.2 Standard Deviation

SD = Standard Deviation of initial 5 RFs for each compound calculated as follows:

$$SD = \sqrt{\sum_{i=1}^{n} \frac{\left(x_i - \overline{x_i}\right)^2}{n-1}}$$

$\overline{x_i}$ = Mean (Average) of initial 5 RFs for each compound.

n = number of standards

x_i = individual RF

11.3 Relative Standard Deviation (%RSD) = $\frac{\mathbf{SD}}{\mathbf{RF_{ave}}} \times \mathbf{100}$

where:

RF_{ave} = The average of the 5 or more initial calibration RFs

SD = The standard deviation of the average RFs

11.4 Response Factors (RF)

$$\mathbf{RF = \frac{Total\ Area\ Response\ within\ RT\ window}{Concentration\ of\ Standard}}$$

Where:

Total Area Response for Multi-component standards includes the area of all designated peaks.

11.5 Percent Difference (%D)

$$\%D = \frac{|RF_{av} - RF_c|}{RF_{av}} \times 100$$

Where:

RF_{av} = The average of the 5 or more initial calibration RFs
RF_c = Continuing calibration RF

11.6 **<u>% Drift Calculation</u>**

% Drift calculation in used for comparing continuing calibration responses to a **linear** curve. The criteria for % Drift is the same as for % Difference.

$$\%Drift = \frac{\text{Calculated concentration - Theoretical concentration}}{\text{Theoretical concentration}} \times 100\%$$

11.7 **Linear Regression**: A linear calibration model based on a least squares regression is employed for analytes that do not meet the RSD limits. This model may also be employed for calibrations that do meet the RSD limits.

For external standard calibration, x is the concentration of the analyte in the sample aliquot introduced into the instrument and y is the area as in:

$x = C_s$ and $y = A_s$

A linear least squares regression attempts to construct a first-order linear equation of the form:

$y = ax + b$

The mathematics used in least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves generated tend to fit points at the upper calibration levels better than points at the lower calibration levels. To compensate for this, a weighting factor which reduces this tendency is used. Examples of acceptable weighting factors which place more emphasis on numbers of smaller value are:

$w = 1/y$ or $w = 1/y^2$

11.8 Coefficient of Determination & Correlation Coefficient

The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995 or r2 >0.99.

Coefficient of Determination **Correlation Coefficient**

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2} \qquad r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response
x = Concentration

11.9 Concentration Calculation

$$\text{Concentration } (\mu g/L \text{ or } \mu g/kg) = (\mu g/mL \text{ instrument readout})\frac{(D)(V_t)(1000)}{V_x \text{ or } W_s}$$

V_t = Total volume of the concentrated extract (mL).

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

RF_{mean} = Mean response factor from the initial calibration (area/concentration).

V_s = Volume of the aqueous sample extracted in mL.

W_s = Weight of sample extracted (g).

11.10 Concentration of Pesticides reported by the Data System (for average curve fits)

$$\textbf{Conc } (\mu g/L) = \frac{(A_{xc})}{(RF_{ave})}$$

Where:

A_{xc} = Total area response in chosen RT window for single peaks or the sum area response of the 4-5 representative peaks for multi- Component compounds

RF_{ave} = Average RF from initial calibration

11.11 Concentration of Pesticides reported by the Data System - using linear regression.

$$Conc_{RAW} = \frac{A_T - b}{a}$$

Where:

A_T = Area of sample peak
b = The intercept
a = Slope of the line (coefficient of x)

11.12 Concentration of Pesticides in Aqueous samples:

$$\textbf{Conc. (µg/L)} = \frac{(C_r)(DF)}{(Vi)}(Vf)$$

Where:

C_r = Concentration reported by the data system in µg/mL.
Vi = Initial volume of sample
Vf = Final volume of extract
DF = Dilution factor

11.13 Concentration of Pesticides in Soil/Sediment samples:

$$\textbf{Conc. (µg/Kg)} = \frac{(C_r)(DF)}{(W_s)(S)}$$

Where:

Cr = Concentration reported by the data system in µg/L.
Ws = Wet Weight of sample extracted, grams
S = Solid fraction, % solids/100 , optional

11.14 Matrix Spike/Matrix Spike Duplicate Percent Recovery or LCS Percent Recovery:

$$\textbf{\%Recovery} = \frac{C - C_X}{(C_{SP})} \times 100$$

Where:

C = Concentration of Pesticide in Matrix Spike, Matrix Spike Duplicate, or LCS
C_X = Concentration of Pesticide in unspiked sample (above MRL, assume 0 for C <MRL)
C_{sp} = Spike level.

This formula is used to calculate LCS recoveries as well. C_x = 0 in the LCS.

11.15 Precision (RPD)

$$RPD = \left[\frac{(V_o - V_d)}{[(V_o + V_d)/2]} \right] x100$$

V_o = Original sample value
V_d = Duplicate sample value

11.16 Endrin/DDT Percent Breakdown

%DDT Breakdown $= \left(\frac{(A_{DDE} + A_{DDD})}{(A_{DDT} + A_{DDE} + A_{DDD})} \right) 100$

Where:

A_{DDT} = Area of DDT Peak

A_{DDE} = Area of DDE Peak

A_{DDD} = Area of DDD Peak

%Endrin Breakdown $= \left(\frac{(A_{EA} + A_{EK})}{(A_E + A_{EA} + A_{EK})} \right) 100$

Where:

A_E = Area of Endrin Peak

A_{EA} = Area of Endrin Aldehyde Peak

A_{EK} = Area of Endrin Ketone Peak

Endrin Ketone Peak

12.0 <u>Method Performance</u>

12.1 <u>Demonstration of Capabilities</u> - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.2 <u>Method Detection Limit Study</u> - A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 The supervisor has responsibility to ensure that an analyst who has been performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.4 Retention time windows - are established initially by injection of three calibration standards over 72 hours. The mean and standard deviation of the retention times are

calculated. A retention time window is established as ± 3 SD from the mean retention time. The absolute RTW must be established for each analyte and surrogate on each column and instrument. New retention time windows must be established when new types of columns are installed. See Table 6 for estimated Retention Times.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in **accordance with all federal and state laws and regulations.** Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.2 The following waste stream is produced when this method is carried out:

- Solvent waste generated by the extraction is collected, drummed and disposed of through a Waste Handler.
- Expired primary and working standards are treated as Solvent Waste.
- Vials containing sample extracts are treated as solvent waste.

15.0 References / Cross-References

15.1 USEPA SW-846, Method 8081, Organochlorine Pesticides by Gas Chromatography, Revision 1, December 1996.

15.2 USEPA SW-846, Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

15.3 USEPA SW-846, Chapter Four, Organic Analytes. Revision 3. December 1996.

15.4 USEPA SW-846, Methods 3510,3520, 3540, 3545, 3600. December 1996.

15.5 DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton.

15.6 DT-QA-005 Procedure for Balance Calibration Check.

15.7 DT-QA-006 Thermometer Calibration.

15.8 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.

15.9 **NOTE:** This is an OVAP approved SOP. Any changes to this procedure must be approved by OVAP prior to implementation.

15.10 CORPORATE QUALITY MEMORANDUM NO. CA-Q-QM-003 - Technical Guidance on Reporting of Multi-Component Organochlorine Analytes

15.11 CA-T-P-002 rev2 Selection of Calibration Points

16.0 Method Modifications

None.

17.0 Attachments

Table 1. Standard Source
Table 2. Preparation of Single Component Calibration Standards
Table 3. Preparation of Toxaphene/Chlordane Calibration Standards
Table 4. Preparation of Endrin/DDT Breakdown Standard
Table 5. LCS/MS/MVS Spikes
Table 6. Estimated Retention Time
Table 7 Example GC Operating Conditions
Table 8 Example Method Reporting Limits

18.0 Revision History

18.1 Revision dates:

- 7/22/11 replaces 9/13/07 (biannual update)
- Revision dated 9/13/2007

18.2 Changes from last revision

SOP Section	Change from	Change to	Reason
Copyright	2007 references	2011 format	Copyright statement is updated annually.
Entire SOP	Reporting Limit (RL)	Method Reporting Limit (MRL)	Consistency throughout SOP and with other SOPs
1.2	added	Additional compounds may be analyzed using this procedure, provided all appropriate quality control measures are evaluated and found acceptable. For OVAP, only compounds listed in the method may be reported using this procedure	
5	NA	New Safety statements were added by EH&S Director	Comply with new statement
6.10	N/A	Allow use of other disposable tubes if properly calibrated.	Allow for more flexibility and ensure analysts are aware that tubes must be calibrated.
8	Outline form	Moved information to Table form.	For consistency with other SOPs.
8.4	Added	* For concrete and other unusual matrices, the samples may be collected	OVAP sop recommendation

SOP Section	Change from	Change to	Reason
		in plastic bottles, plastic bags or other containers.	
9	Outline form	Moved information to Table form.	For consistency with other SOPs.
9.4.3	Added	The LCS may be spiked with and/or evaluated for a limited list of target analytes, provided this is acceptable to the regulatory program for which samples are being analyzed.	Clarification of requirements
9.6	added	For Ohio VAP: The laboratory must implement corrective action procedures to resolve the deviation and limit qualification of the final results. The laboratory is not permitted to deviate from its VAP approved SOP if it intends to attest under affidavit that the "results" are VAP certified. When all corrective actions listed in the SOP have been exhausted, it may be necessary to use technical judgment in which case the decision process and rationale will be presented in the final report and/or affidavit **and the data will be noted as 'not VAP certified' on the affidavit.**	OVAP SOP requirement
Entire SOP	Added	Corrective action language	OVAP Sop requirements
10.6	Added	See body of SOP for text regarding Selection of Calibration Points	SOP Clarification
10.9.5, 10.9.6	Added	See body of SOP for text regarding second column qualitative and quantitative confirmation	SOP Clarification, change in confirmation procedure
10.9.6 bullet 4	If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the higher result- unless	If no chromatographic interference is noted, report the higher value unless - unless otherwise specified in an approved	

SOP Section	Change from	Change to	Reason
	otherwise specified in an approved project plan. Qualify the data to indicate the disparity in the results. **For OVAP, always report the higher value, qualification of results for >40% RPD is not required**	project plan. Qualify the data to indicate the disparity in the results.	
13 & 14	Section 13	Previous section 13 was split into two sections.	For consistency with other SOPs.
15	N/A	• DT-QAM-001Quality Assurance Manual for TestAmerica Dayton • DT-QA-005 Procedure for Balance Calibration Check • DT-QA-006 Thermometer Calibration • DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus	NELAC (PA 2009 audit) requires the reference of these ancillary SOPs.
19	N/A	Move information regarding OVAP from section 19 to references Section 15.	For consistency with other SOPs. Section 19 is not present in non-VAP sops.

Table 1: Standard Sources

	Calibration Standards		*Verification Standards*	
Analyte	**Conc. (µg/mL)**	**Solvent**	**Conc. (µg/mL)**	**Solvent**
Aldrin	200	Hexane/Toluene	1000	Hexane/Toluene
α-BHC	200	Hexane/Toluene	1000	Hexane/Toluene
β-BHC	200	Hexane/Toluene	1000	Hexane/Toluene
δ-BHC	200	Hexane/Toluene	1000	Hexane/Toluene
γ-BHC (Lindane)	200	Hexane/Toluene	1000	Hexane/Toluene
α-Chlordane	200	Hexane/Toluene	1000	Hexane/Toluene
γ-Chlordane	200	Hexane/Toluene	1000	Hexane/Toluene
4,4'-DDD	200	Hexane/Toluene	1000	Hexane/Toluene
4,4'-DDE	200	Hexane/Toluene	1000	Hexane/Toluene
4,4'-DDT	200	Hexane/Toluene	1000	Hexane/Toluene
Dieldrin	200	Hexane/Toluene	1000	Hexane/Toluene
Endosulfan I	200	Hexane/Toluene	1000	Hexane/Toluene
Endosulfan II	200	Hexane/Toluene	1000	Hexane/Toluene
Endosulfan sulfate	200	Hexane/Toluene	1000	Hexane/Toluene
Endrin	200	Hexane/Toluene	1000	Hexane/Toluene
Endrin aldehyde	200	Hexane/Toluene	1000	Hexane/Toluene
Endrin ketone	200	Hexane/Toluene	1000	Hexane/Toluene
Heptachlor	200	Hexane/Toluene	1000	Hexane/Toluene
Heptachlor epoxide	200	Hexane/Toluene	1000	Hexane/Toluene
Hexachlorobenzene	200	Hexane/Toluene	1000	Hexane/Toluene
Methoxychlor	200	Hexane/Toluene	1000	Hexane/Toluene

Multi-component Standards:

Chlordane, Technical*	1000	Hexane	1000	Isooctane
Toxaphene *	1000	Hexane	1000	Isooctane

Surrogates:

Decachlorobiphenyl	200	Acetone	200	Acetone
Tetrachloro-m-xylene	200	Acetone	200	Acetone

Breakdown Standard:

4,4'-DDT/Endrin	500	Methanol	Not applicable

Table 2: Preparation of Single Component Calibration Standards

Cal. Standard	Pesticide Conc. (µg/L)	Surrogate Conc. (µg/L)	Cal. Stock in 100 mL (µL)	Surr. Stock in 100 mL (µL)
CAL 1	10	2	5	1
CAL 2	20	4	10	2
CAL 3	50	10	25	5
CAL 4	80	16	40	8
CAL 5	100	20	50	10
CAL 6	160	40	80	20
ICV	50	10	25	5

CCV is made at mid-level, usually CAL 3 or CAL4

Standards may be prepared and used at other concentrations, but there must be a standard in the calibration curve at or below the concentration of the Method Reporting Limit. A minimum of 5 points must be use for initial calibration.

Table 3: Preparation of Toxaphene/Chlordane Calibration Standards

Cal. Standard	Toxaphene Conc. (µg/L)	Chlordane Conc. (µg/L)	Surrogate Conc. (µg/L)	Toxaphene Stock (1000 µg/mL in 50 mL) (µL)	Chlordane Stock (1000 µg/mL in 50 mL) (µL)	Surr. Stock (200 µg/mL in 50 mL) (µL)
CAL 1	20	20	4	1	1	1
CAL 2	50	50	10	2.5	2.5	2.5
CAL 3	100	100	20	5	5	5
CAL 4	200	200	40	10	10	10
CAL 5	400	400	80	20	20	20
ICV	100	100	20	5	5	5

CCV is made at mid-level, usually CAL 3 or CAL4

Standards may be prepared and used at other concentrations, but there must be a standard in the calibration curve at or below the concentration of the Method Reporting Limit. A minimum of 5 points must be use for initial calibration.

Note: All ICV are prepared from a second source separate from the calibration standards.

This source is the same as for the LCS/MS/MSD.

Table 4: Preparation of Endrin/DDT Breakdown Standard

	Volume of Standard(µL)	Final Conc. in Standard (µg/mL)	Final Volume
Supelco DDT/Endrin Mix	20		50mL
Hexane	to volume	n/a	
DDT		500	
Endrin		500	

Table 5: MS, LCS, MVS Spikes

Analyte	Spike** (µg/L)
Aldrin	50
α-BHC	50
β-BHC	50
δ-BHC	50
γ-BHC (Lindane)	50
Chlordane, Technical*	N/A
α-Chlordane	50
δ-Chlordane	50
4,4'-DDD	50
4,4'-DDE	50
4,4'-DDT	50
Dieldrin	50
Endosulfan I	50
Endosulfan II	50
Endosulfan sulfate	50
Endrin	50
Endrin Aldhyde	50
Endrin Ketone	50
Heptachlor	50
Heptachlor epoxide	50
Hexachlorobenzene	50
Methoxyclor	50
Surrogate: Decachlorobiphenyl	20
Surrogate: Tetrachloroxylene	20

Standards may be prepared and used at other concentrations, but there must be a standard in the calibration curve at or below the concentration of the Method Reporting Limit. A minimum of 5 points must be use for initial calibration.

**1L of LCS/MS/MSD is spiked with 1mL of 0.5µg/mL aqueous spike or 10 g of soil is spiked with 0.5 mL of 5µg/mL soil spike and concentrated to 10 mL (aqueous) or 50 mL (soil), yielding the final extract concentrations stated above.

Table 6: Estimated Pesticide Retention Times

	Rtx-CLPest (min)	Rtx-CLPest (min)
Aldrin	6.78	6.78
α-BHC	5.40	5.41
β-BHC	5.91	5.96
δ-BHC	6.13	6.32
γ-BHC (Lindane)	5.79	5.84
Chlordane, Technical*	MP	MP
α-Chlordane	7.98	8.04
γ-Chlordane	7.79	7.83
4,4'-DDD	9.00	9.19
4,4'-DDE	8.13	8.33
4,4'-DDT	9.41	9.65
Dieldrin	8.51	8.51
Endosulfan I	8.16	8.11
Endosulfan II	9.18	9.27
Endosulfan sulfate	10.50	10.23
Endrin	8.84	8.94
Endrin aldehyde	9.82	9.80
Endrin ketone	10.91	11.04
Heptachlor	6.40	6.38
Heptachlor epoxide	7.62	7.57
Hexachlorobenzene	5.18	5.21
Methoxychlor	10.20	10.78
Toxaphene *	MP	MP

*Multi-component mixtures

Table 7: Example GC Operating Conditions

Carrier gas	Hydrogen
Carrier gas flow rate	52 cm/sec
Makeup gas	Nitrogen
Makeup gas flow rate	70 cm/sec
Injector temperature	200 ^{o}C
Detector temperature	325 ^{o}C
Initial temperature	120 ^{o}C
Initial time	1 min
Temperature program	120 ^{o}C to 200 ^{o}C @20 ^{o}/min, 200 to 300 ^{o}C @ 10 ^{o}C/min Hold at 300 ^{o}C for 2 min.
Final temperature	200 ^{o}C
Injection volume	1 µL
EPC:	
Constant Flow	On
Initial Pressure	7.5 psi
Purge Valve On Time	0.75 min

Table 8: Example Method Reporting Limits

Analyte	Conc. (µg/L)	Conc. (µg/Kg)
Aldrin	0.10	50
α-BHC	0.10	50
β-BHC	0.10	50
δ-BHC	0.10	50
γ-BHC (Lindane)	0.10	50
α-Chlordane	0.10	50
γ-Chlordane	0.10	50
4,4'-DDD	0.10	50
4,4'-DDE	0.10	50
4,4'-DDT	0.10	50
Dieldrin	0.10	50
Endosulfan I	0.10	50
Endosulfan II	0.10	50
Endosulfan sulfate	0.10	50
Endrin	0.10	50
Endrin aldehyde	0.10	50
Endrin ketone	0.10	50
Heptachlor	0.10	50
Heptachlor epoxide	0.10	50
Hexachlorobenzene	0.10	50
Methoxychlor	0.10	50
Chlordane	0.20	100
Toxaphene	0.20	300

Title: PolyChlorinated Biphenyls (PCBs)

USEPA SW-846 Method 8082, Revision 0, December 1996.

Approvals (Signature/Date):

2/18/2011 Josh McKinney — Date Department Manager	2/18/2011 Jason Lykins — Date EH&S Officer
2/18/2011 Violet Fanning — Date Quality Assurance Manager	2/192011 Tara Schlenker — Date Laboratory Director

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1.0 Scope and Application

1.1 Method 8082 is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from various solid and liquid matrices, using fused silica, open-tubular, capillary columns with electron capture detectors (ECD). When compared to the packed columns, these columns offer improved resolution, better selectivity, increased sensitivity, and faster analysis. The compounds listed in Table 1 may be determined by either a single- or dual-column analysis system.

1.2 Non-Aqueous Samples are prepared using Pressurized Fluid Extraction (3545) and/or Waste Dilution (3580A). Aqueous samples are prepared using Liquid-Liquid Continuous (3520), and/or Separatory Funnel (3510).

1.3 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards.

1.4 Compound identification based on single-column analysis must be confirmed on a second column, or must be supported by at least one other qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm the measurement made with the primary column. GC/MS Method 8270 is also recommended as a confirmation technique when sensitivity permits.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.6 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis as indicated in the QAManual. **OVAP does not allow modifications to the SOP.**

2.0 Summary of Method

2.1 A measured volume or weight of sample (approximately 1 L for liquids, approximately 10 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) that will destroy most organic chemicals and/or a copper powder or tetrabutylammonium sulfite (TBA) clean up that is effective for elemental sulfur.

2.3 After cleanup, the extract is analyzed by injecting a sample into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector.

3.0 Definitions

3.1 DCB - Surrogate Decachlorobiphenyl.

3.2 TCX - Surrogate Tetrachloro-m-xylene

3.3 Primary and Secondary Column – The primary column refers to the column which is normally used for quantitation. The secondary column is normally used for qualification only. Either column can be used for quantitation and reporting if it meets the criteria.

3.4 Please see the glossary in TestAmerica Dayton's Quality Assurance Manual (Document number DT-QAM-001) for definitions.

4.0 Interferences

4.1 Sources of interference in this method can be grouped into three broad categories.

4.1.1 Contaminated solvents, reagents, or sample processing hardware.

4.1.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

4.1.3 Compounds extracted from the sample matrix to which the detector will respond. Interferences co-extracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

4.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. Common flexible plastics contain varying amounts of phthalate esters that are easily extracted or leached from such materials during laboratory operations. This interference can best be minimized by avoiding contact with plastic materials and checking all solvents and reagents for phthalate contamination. Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

4.3 Glassware must be scrupulously cleaned. Extraction glassware is detergent washed with hot water and rinsed with tap water and organic-free reagent water. This is followed by Methylene chloride and methanol rinses.

4.4 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting Aroclors. Sulfur contamination should be expected with sediment samples. Method 3660 is suggested for removal of sulfur.

4.5 Halogenated pesticides or other industrial chemicals may interfere with the analysis of Aroclors, particularly the multi-component analytes such as Chlordane or Toxaphene.

4.6 Poor GC performance may be expected when a chromatographic system is contaminated with high boiling point materials, particularly in the injector. Routine maintenance should be performed such as replacement of septa, metal seals, liners and removing as much as 0.5 – 1 M from the injector side of the capillary column.

4.7 Carrier gas should be scrubbed to remove traces of oxygen and scrubbers should be changed regularly. Carrier gas should always be passed through the column whenever the oven is heated

4.8 When there are numerous PCB peaks present but there are no good matches to any individual Aroclor, choose the Aroclor (or Aroclors) that most closely match the sample and quantify the peaks as that Aroclor. The sample should not be reported as "not detected" based solely on the absence of a good match to a single Aroclor mixture.

Multiple Aroclors should only be reported if their patterns are reasonably well separated. For example, 1232 and 1254 could be reported together, but not 1242 and 1248.

When we are reporting and quantifying PCBs that do not closely match an Aroclor standard, it is absolutely essential and mandatory that we explain this in the report narrative.

Some clients may insist on ND reporting if the patterns are not clear. In that event, we should add information to the project file to indicate that the information in this guidance have been communicated to the client, together with the client's instructions. **In addition,**

in the event of a poor match to patterns, we would still insist on a narrative as suggested in the previous paragraph.

Reference - CA-Q-QM-003 - Technical Guidance on Reporting of Multi-Component Organochlorine Analytes

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), 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

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

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
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

Sylon-CT (5% in Toluene)	Flammable Carcinogen Teratogen Reproductive hazard Severe eye irritant Skin irritant	Toluene 200 ppm PEL 200 ppm TWA Ceiling 500 Maximum	May cause respiratory track irritation. Vapors may cause drowsiness or dizziness. Exposure to the eyes will cause severe irritation.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Gas chromatograph: an analytical system complete with gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, autosamplers, electron capture detectors (ECD), and data system. It is recommended that the system be equipped with two ECDs. The Agilent Technologies Model 5890 or 6890 is preferred.

6.2 The data acquisition system must be capable of time stamping all data produced with the correct date and time. If regression is to be used in place of average response factor calibration, the system must be capable of plotting the curves and calculating correlation coefficients.

6.3 GC columns. The following pairs of columns can be used:

- Restek Rtx-CLP 30m, 0.32mm ID, 0.50µm (Cat. #11139)
- Restek Rtx-CLP2 30m, 0.32mm ID, 0.25µm (Cat. #11324)

6.4 5 µL or 10-µL autosampler syringes.

6.5 Restek Siltek single gooseneck injection port liners.

6.6 Restek Ice Blue Injection port septa.

6.7 Restek Siltek injection port seals.

6.8 Class A Volumetric flasks of varying concentrations for preparation of standards.

6.9 Micro syringes of varying volumes for preparation of standards and dilution of samples.

6.10 Amber 2 mL crimp top vials with crimp caps.

6.11 Reagent bottles for standards storage. Caps must be Teflon-lined.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

7.1 All stock standard solutions must be replaced after one year or sooner if routine QC tests indicate a problem. All other standard solutions must be replaced after six months or sooner if routine QC indicates a problem. All standards must be stored at <6.0^{o} C but not frozen.

7.2 Organic-free reagent water.

7.3 All solvents must be stored at room temperature in appropriate storage area.

7.3.1 n-Hexane, pesticide grade or better.

7.3.2 Acetone, pesticide grade or better.

7.3.3 Methylene chloride, pesticide grade or better.

7.3.4 Methanol, reagent grade or pesticide grade.

7.4 Calibration standards. See Table 2, 3, and 4. Prepare as indicated in cited tables by adding amounts of standards to a partially filled volumetric flask and then bringing to final volume with appropriate solvent.

7.5 ICV Standard. See Table 2 for Standard source. This standard is prepared from a source separate from the calibration standards. The ICV may be prepared from the same source as the LCS, but not necessarily at the same concentrations.

7.6 Supelco Sylon CT 5% for silanization of standards glassware.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Preferred Sample Container	Suggested Sample Size	Preservation	Holding Time	Reference
Aqueous	1L (or 1gal) amber glass with Teflon-lined lids	1L	Cool <6.0°C, but not frozen	1 year from collection to extraction	SW 846 & 40CFR
Non-aqueous	Glass with Teflon-lined lids.*	20 g	Cool <6.0°C, but not frozen	1 year from collection to extraction	SW 846 & 40CFR
Extracts	n/a	n/a	Cool <6.0°C, but not frozen, store in dark	1 year from extraction to analysis	SW 846 & 40CFR

8.2 All samples and sample extracts are stored separately from standards.

*For concrete and other unusual matrices, the samples may be collected in plastic bottles, plastic bags or other containers.

9.0 Quality Control

9.1 The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Acceptance Limits
Method Blank (MB)	1 per preparation batch[1]	<RL.
Laboratory Control Sample (LCS)	1 per preparation batch[1]	Historic limits are maintained in LIMSs
Matrix Spike (MS)[2]	1 per preparation batch[1]	Historic limits are maintained in LIMSs. MS is not used for batch control.
Matrix Spike Duplicate (MSD)[2]	1 per preparation batch[1]	Historic limits are maintained in LIMSs. MSD is not used for batch control.
Surrogates	All samples and QC	Historic limits are maintained in LIMSs

[1]A preparation batch is limited to 20 samples.

[2]The MS/MSD are randomly selected, unless specifically requested by a client.

9.2 **Method Blank** - A method blank must be included with every extraction batch but not necessarily every instrument run batch.

9.2.1 Typically, the method blank is analyzed prior to sample analysis to insure the chromatographic system is contaminant-free.

9.2.2 When samples that are extracted together are analyzed on separate instruments or on separate analytical shifts, the method blank associated with those samples (e.g., extracted with the samples) must be analyzed on at least one of those instruments.

9.2.3 Acceptance criteria is <RL. If the method blank shows a detection above the required reporting limit, it must be reanalyzed. If this fails to correct the problem, all associated samples with concentrations above the reporting limit, for that analyte, must be re-extracted.

- If the associated samples are non-detect, then reanalysis of the Method Blank is not required and re-extraction of samples is not required.
- If the concentration found in the samples is >10X the concentration found in the Method Blank, reanalysis is not required, but data must be flagged. **This exception is not allowed by OVAP.**
- The laboratory must not subtract results of the method blank from those of any associated samples. Such “blank subtraction” is inappropriate.
- Method blanks may be used to check contamination by carryover from a high-concentration sample into subsequent samples. If the analytes in the high-concentration sample are not present in the subsequent blank, then lack of carryover has been demonstrated.

9.3 Laboratory Control Standard (LCS) – A LCS is extracted with each extraction batch. If the LCS does not pass acceptance limits for any analyte, all samples extracted with the failed LCS must be re-extracted and re-analyzed.

9.3.1 However if the LCS recovery is high for a target, and the associated samples are <RL for that target, the results may be reported.

9.4 **Matrix Spike/Matrix Spike Duplicate (MS/MSD)** - When adequate sample is provided, a set of client samples are spiked with the LCS spike described above to demonstrate any matrix interferences.

9.4.1 If MS/MSD recovery or RPD is out of limits, the parent and MS/MSD must be flagged.

9.4.2 The MS/MSD is not used for batch control.

9.5 **Surrogates** – All samples and standards are spiked with two surrogates. For PCBs, only the surrogate DCB is evaluated, unless there is an interference with the DCB. If there is a chromatographic interference with the DCB, then the TCX may be reported in its place.

9.5.1 Established limits are maintained in the LIMS.

9.5.2 Any sample, including batch QC, with surrogates outside the control limits requires evaluation by the laboratory. Once the problem has been identified and addressed, corrective action must include the reanalysis of samples, the extraction and analysis of new sample aliquots, or qualification of data if corrective action can not be performed due to lack of sample, hold time exceedence or other issues.

9.5.3 The laboratory must re-extract all associated samples when an extraction batch method blank or LCS contains a surrogate outlier (OVAP program).

9.5.4 If the blank, LCS or individual sample surrogate recoveries are high, and the associated analytes are non-detect, then reanalysis and/or re-extraction is not necessary. As this would have no impact on the sample data, data qualification is not necessary, but may be required for some regulatory programs.

10.0 Procedure

10.1 **Extract cleanup** – Cleanup procedures may not be necessary for a relatively clean sample matrix, but some extracts from environmental and waste samples require additional preparation before analysis. The specific cleanup procedure used depends on the nature of the sample to be analyzed and the data quality objectives for the measurements.

10.1.1 Method 3665 (sulfuric acid/potassium permanganate) may be used to remove many single component organochlorine or organophosphorus pesticides.

10.1.2 Elemental sulfur, which may be present in certain sediments and industrial wastes, interferes with the electron capture gas chromatography of certain pesticides. Sulfur should be removed by the technique described in Method 3660.

10.2 **GC Conditions**

10.2.1 Single-column analysis was selected with the use of two narrow bore capillary columns each attached to separate injector systems.

10.2.2 Table 5 lists the GC operating conditions for the single-column method of analysis.

10.2.3 Because of the low concentration of PCB standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day or more. GC column should be primed (or deactivated) by injecting a PCB standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

10.3 **12-Hour Run Batch** - is initiated with the injection of the first calibration standard or CCV. The batch may include as many injections as can be made within 12 hours of the injection of the CCV or first standard up to a maximum of 20 client samples. The batch

must be concluded with a post-run CCV. Any sample analyzed outside the 12-hour clock must be re-analyzed.

10.4 **Initial Calibration (periodic)** - The initial calibration involves the analysis of standards containing Aroclors 1016 and 1260 at a minimum of five different concentrations. All other Aroclors are analyzed using a single point calibration at a concentration near the midpoint of the 1016/1260 curve. The initial calibration establishes the working range of the instrument and the lowest level standard determines the reporting limit. The extrapolation of the calibration to concentrations above or below those of the actual calibration is **not** appropriate.

10.4.1 Prepare and analyze a minimum of five calibration standards containing a mixture of Aroclor 1016 and Aroclor 1260 as described in Table 3. This mixture includes many of the peaks represented in the other five Aroclor mixtures and can thus be used to demonstrate detector linearity.

10.4.2 A minimum of 3 characteristic peaks must be chosen for each Aroclor, at least one of which should be unique to the Aroclor in question and the remaining peaks should be consistent with the peaks selected for 1016 and 1260.

10.4.3 If the relative standard deviation **(RSD**) of the calibration is 20% or less, linearity through the origin may be assumed and average response factors may be used.

10.4.4 RSDs, RFs and other criteria are based on the average response of all peaks used with that aroclor, as opposed to the individual response for each peak. See example in 10.4.7.1

10.4.5 Alternatively, a regression equation may be utilized and the correlation coefficient (r) must be greater than or equal to 0.99. (Enviroquant measures r^2, which must be greater than or equal to 0.980). See Section 11 for the calculation.

10.4.6 If the RSD for any analyte is greater than 20% (or r>0.99) and the problem appears to be associated with a single standard, that one standard may be reanalyzed and the calibration reevaluated provided no samples have been analyzed.

10.4.7 Initial calibration curves must be re-run if the CCV criteria is not met and each time a significant change is made to the analytical system (A significant change would include installation of new columns or detectors or change in temperature program but would not include the changes made from daily maintenance such as replacing a septa or liner or trimming of the analytical column.)

10.4.7.1 Criteria for calibration curves, CCVs, sample results and other QC results is based on the average response of all peaks used with that aroclor, as opposed to the individual response from each peak. For example:

Aroclor ID	RSD
Aroclor 1242 (peak 1):	10%
Aroclor 1242 (peak 2):	15%
Aroclor 1242 (peak 3):	20%
Aroclor 1242 (peak 4):	12%
Aroclor 1242 (peak 5):	25%
Aroclor 1242 (average):	16.4%

10.4.8 Unless otherwise necessary for a specific project, the analysis of Aroclors 1221, 1232, 1242, 1248 and 1254 employ a single-point calibration. A single calibration standard of each multi-component standard near the mid-point of the calibration range used for 1016/1260 is included with the initial calibration of Aroclors 1016 and 1260 for pattern recognition, so that the analyst is familiar with the patterns and retention times on each column. Quantitation of the other five Aroclors is performed using a minimum of three peaks. RF is calculated by summing the area of the peaks. See Section 11 for the calculation. If a multi-point calibration was performed for any of these individual Aroclors, use the RF calculated from those standards to evaluate linearity.

10.4.8.1 If the RSDs for the 1016/1260 are <20%, then linearity has been established and the RFs for the single point aroclors may be used for quantitation of samples- regardless of the curve fit applied to the 1016/1260. However, if the 1016/1260 RSDs are >20%, then linearity has not been established and the single points must not be used to quantify samples- a 5 point calibration curve is required.

10.4.9 Reference chromatograms for Aroclors 1262 & 1268 are kept on file. The Laboratory does not calibrate for these Aroclors, but if found in samples they are quantitated as 1260 and narrated. **The Laboratory is not approved to analyze for 1262 & 1268 for OVAP.**

10.5 **Initial Calibration Verification (ICV)** – A standard from a source independent of the calibration standards is analyzed following every initial calibration curve. The quantitated results of the ICV must be within ± 30% of the true concentration of each analyte and surrogate in the ICV. The ICV may be used as a CCV but must meet the more strict criteria outlined in

10.5.1 If the ICV fails criteria, investigate to determine the source of the problem. If the issue is with the standard used to prepare the ICV or if the ICV was prepared incorrectly, prepare a new ICV and reanalyze. If the reanalyzed ICV is still unacceptable, then additional corrective action is required. Additional corrective must include at least the reanalysis of the initial calibration curve and ICV.

- However, if the ICV exhibits a response for an analyte that is <u>above</u> the acceptance limit and the analyte was <u>not</u> detected in the samples, then the extracts for those samples do not need to be reanalyzed and may be reported.

10.6 **Continuing Calibration (Daily)**

10.6.1 <u>Continuing Calibration Verification (CCV)</u> – Verify the calibration each 12-hour shift by injecting a CCV prior to conducting any sample analyses. A CCV must be injected at intervals of not less than once every 20 client samples and at the end of the analysis sequence. Note that injection of method blanks, LCSs, MS/MSDs or solvent blanks are not included in the 20-sample count.

10.6.2 When using an average curve fit, evaluate the % difference from the mean Response Factor calculated for the initial calibration(expressed as the aggregate of the peaks used for quantitation) When using regression, evaluate the % Drift . Acceptance criteria is±15% of the true value, ±30% for surrogates. See Section 11 for the calculations.

10.6.3 All samples must be bracketed with CCVs that meet these acceptance criteria.

10.6.4 When a CCV fails to meet the QC criteria, all samples that were injected after the last CCV that passed must be re-injected.

- However, if the CCV exhibits a response for an analyte that is above the acceptance limit (>15%) and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed and may be reported

10.6.5 The first CCV of the run is also used to establish each analyte and surrogate retention time for the12-hour clock. (Daily maintenance of the GC may include removing a portion the column. This action may result in a shift of retention times). However, if any subsequent CCV in the analytical sequence has an analyte which does not fall within its determined retention time window, the run is out of control and corrective action must be performed.

10.7 **Sample Analysis**

10.7.1 Samples and Extraction batch QC can only be analyzed following successful calibration verification. Generally, it is advisable to analyze the extraction method blank and LCS prior to sample analysis.

10.7.2 Proper quantitation requires the appropriate selection of a baseline from which the peak area can be determined. For concentration calculations see Sections 11.

10.7.3 If the responses exceed the calibration range of the system, dilute the extract and re-analyze.

10.7.4 Identification of Aroclors is based on the characteristic “fingerprint” retention time and shape of the indicator peaks. Quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peaks of the same retention time and shape generated using an external calibration procedure.

10.7.5 Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. In these cases, quantitation is performed on the basis of the Aroclor standard that is most similar to the sample.

10.7.6 Second column confirmation is required for any detections in samples. The second column must meet the same initial calibration and daily verification criteria as the primary column.

- When the sample results are confirmed using two dissimilar columns, the agreement between the quantitative results must be evaluated after the identification has been confirmed.
- Calculate the relative percent difference (RPD) as described in Section 11. If one result is significantly higher (e.g. >40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result. If no overlapping peaks are noted, examine the baseline parameters established by the instrument data system (or operator) during peak integration.
- If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the higher result unless otherwise specified in an approved project plan. Qualify the data to indicate the disparity in the results. For OVAP, always report the higher value, qualification of results for >40% RPD is not required.
- When samples are analyzed from a source known to contain specific Aroclors, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern. This approach should

not be attempted for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors. In order to employ this approach, the analyst must document the source-specific information indicating that Aroclors are anticipated in the sample (historical data, generator knowledge…)

11.0 Calculations / Data Reduction

PCBs as analyzed by this procedure exhibit a linear response. As such, Quadratic fits have been determined to be inappropriate for this analysis.

11.1 Accuracy = **Concentration detected** / **Concentration spiked** **x 100**

11.2 **Standard Deviation**

SD = Standard Deviation of initial 5 RFs for each compound calculated as follows:

$$SD = \sqrt{\sum_{i=1}^{n} \frac{\left(x_i - \overline{x_i}\right)^2}{n-1}}$$

$\overline{x_i}$ = Mean (Average) of initial 5 RFs for each compound.

n = number of standards

x_i = individual RF

11.3 Relative Standard Deviation (%RSD) = **SD** / **RF_{ave}** **x 100**

where:

RF_{ave} = The average of the 5 or more initial calibration RFs

SD = The standard deviation of the average RFs

11.4 Response factors (RF) = **Total Area Response within RT window** / **Concentration of Standard**

11.5 Percent Difference (%D) = **| RF_{av} - RF_c | / RF_{ave} x 100**

where:

RFav = The average of the 5 or more initial calibration RFs

RFc = Continuing calibration RF

11.6 % Drift Calculation

% Drift calculation in used for comparing continuing calibration responses to a **linear** curve. The criteria for % Drift is the same as for % Difference.

$$\%\text{Drift} = \frac{\text{Calculated concentration - Theoretical concentration}}{\text{Theoretical concentration}} \times 100\%$$

11.7 **Linear Regression**: A linear calibration model based on a least squares regression is employed for analytes that do not meet the RSD limits. This model may also be employed for calibrations that do meet the RSD limits.

For external standard calibration, x is the concentration of the analyte in the sample aliquot introduced into the instrument and y is the area as in:

$x = C_s$ and $y = A_s$

A linear least squares regression attempts to construct a first-order linear equation of the form:

$y = ax + b$

The mathematics used in least squares regression has a tendency to favor numbers of larger value over numbers of smaller value. Thus the regression curves generated tend to fit points at the upper calibration levels better than points at the lower calibration levels. To compensate for this, a weighting factor which reduces this tendency is used. Examples of acceptable weighting factors which place more emphasis on numbers of smaller value are:

$w = 1/y$ or $w = 1/y^2$

11.8 Coefficient of Determination & Correlation Coefficient

The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.995 or r2 >0.99.

Coefficient of Determination

$$r^2 = \frac{\left(\sum xy\right)^2}{\sum x^2 \sum y^2}$$

Correlation Coefficient

$$r = \frac{\left(\sum xy\right)}{\sqrt{\sum x^2 \sum y^2}}$$

y = Response
x = Concentration

11.9 **Concentration Calculation**

$$\text{Concentration } (\mu g/L \text{ or } \mu g/kg) = \frac{(\mu g/mL \text{ instrument readout})(D)(V_t)(1000)}{V_x \text{ or } W_s}$$

V_t = Total volume of the concentrated extract (mL).

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

RF_{mean} = Mean response factor from the initial calibration (area/concentration).

V_s = Volume of the aqueous sample extracted in mL.

W_s = Weight of sample extracted (g).

11.10 Extract (raw) concentration- using average curve fit

$$\textbf{Conc } (\mu g/L) = \frac{(A_{xc})}{(RF_{ave})}$$

where:

A_{xc} = Area response

RF_{ave} = Average RF from initial calibration

11.11 Extract (raw) concentration- using linear regression.

$$Conc_{RAW} = \frac{A_T - b}{a}$$

Where:

A_T = Area of sample peak

b = The intercept

a = Slope of the line (coefficient of x)

11.12 Concentration in Aqueous samples:

$$\textbf{Conc. } (\mu g/L) = \frac{(C_r)(DF)}{(Vi)}(Vf)$$

Where:

C_r = Concentration reported by the data system in µg/mL.

Vi = Initial volume of sample

Vf = Final volume of extract

DF = Dilution factor

11.13 Concentration in Soil/Sediment samples:

$$\textbf{Conc. (µg/Kg)} = \frac{(C_r)(DF)}{(W_s)(S)}$$

Where: C_r = Concentration reported by the data system in µg/L.
W_s = Wet Weight of sample extracted, grams
S = Solid fraction, % solids/100 , optional

11.14 Matrix Spike/Matrix Spike Duplicate Percent Recovery or LCS Percent Recovery:

$$\textbf{\%Recovery} = \frac{C - C_X}{(C_{SP})} \times 100$$

where:
C = Concentration of Aroclor in Matrix Spike, Matrix Spike Duplicate, or LCS
C_X = Concentration of Aroclor in unspiked sample
C_{sp} = Spike level.

This formula is used to calculate LCS recoveries as well. C_x = 0 in the LCS.

11.15 Precision (RPD)

$$RPD = \left[\frac{(V_o - V_d)}{[(V_o + V_d)/2]} \right] x100$$

V_o = Original sample value
V_d = Duplicate sample value

12.0 Method Performance

12.1 Demonstration of Capabilities - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.2 Method Detection Limit Study - A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 The supervisor has responsibility to ensure that an analyst who has been performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.4 Retention time windows. Retention time windows are established initially by injection of three calibration standards over 72 hours. The mean and standard deviation of the retention times are calculated. A retention time window is established as ± 3 Standard

Deviations from the mean retention time. The absolute retention time window must be established for each Aroclor peak and surrogate on each column and instrument. New retention time windows must be established when new types of columns are installed.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in **accordance with all federal and state laws and regulations.** Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.2 The following waste stream is produced when this method is carried out:

14.2.1 Acidic waste generated in the lab is neutralized and discharged into the sanitary sewer.

14.2.2 Solvent waste generated by the extraction is collected, drummed and disposed of through a Waste Handler.

14.2.3 Expired primary and working PCB standards >50ppm are collected, drummed and disposed of through a Waste Handler.

14.2.4 Vials containing sample extracts are treated as solvent waste.

15.0 References / Cross-References

15.1 USEPA SW-846, Method 8082, Polychlorinated Biphenyls (PCBs) by Gas Chromatography, Revision 0, December 1996.

15.2 USEPA SW-846, Method 8000B, Determinative Chromatographic Separations, Revision 2, December 1996.

15.3 USEPA SW-846, Chapter Four, Organic Analytes. Revision 3. December 1996.

15.4 USEPA SW-846, Methods 3510,3520, 3540, 3545, 3600. December 1996.

15.5 DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton.

15.6 DT-QA-005 Procedure for Balance Calibration Check.

15.7 DT-QA-006 Thermometer Calibration.

15.8 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.

15.9 **NOTE:** This is an OVAP approved SOP. Any changes to this procedure must be approved by OVAP prior to implementation.

15.10 CORPORATE QUALITY MEMORANDUM NO. CA-Q-QM-003 - Technical Guidance on Reporting of Multi-Component Organochlorine Analytes

16.0 Method Modifications

None.

17.0 Attachments

Table 1. Example Reporting Limits
Table 2. PCB Standard Sources
Table 3. Preparation of Calibration Standards
Table 4. Preparation of Single Point Calibration Standards
Table 5. Recommended Operating Conditions

18.0 Revision History

18.1 Revision dates

18.1.1 02/22/2011 biannual update
18.1.2 Revision dated 9/12/07

Item	Change from	Change to	Reason
Copyright	2007 references	2011 format	Copyright statement is updated annually.
1.1	…in extracts from solid and liquid matrices,	…in extracts from various solid and liquid matrices,	Various matrices indicates that
1.2	… Ultrasonic Extraction The Laboratory is not approved to analyze OVAP samples via Separatory Funnel or Ultrasonic Extraction.	Removed Removed	The lab is not currently performing Ultrasonic extraction The lab has been approved to perform Sep funnel extraction for PCBs. Ultrasonic extraction is no longer listed in the SOP, so VAP exclusion is redundant.
1.6	On occasion clients may request slight modifications to this SOP. these modifications are addressed on a case by case basis with the supporting demonstration of sensitivity and accuracy (e.g. MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into project special instructions (e.g. Quality Assurance Project Plans), authorized by the laboratory, and mentioned in the report narrative. **OVAP does not allow modifications to the SOP.**	On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis as indicated in the QAManual. . **OVAP does not allow modifications to the SOP.**	
2.1	(approximately 1 L for liquids, 10 g for solids)	(approximately 1 L for liquids, approximately 10 g for solids)	

Item	Change from	Change to	Reason
2.2	…cleanup (Method 3665) designed specifically for these analytes.	…cleanup (Method 3665) that will destroy most organic chemicals and/or a copper powder or tetrabutylammonium sulfite (TBA) clean up that is effective for elemental sulfur. designed specifically for these analytes.	
2.3 (previously)	A variety of additional cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes. Suggested cleanups include alumina (Method 3610), Florisil (Method 3620), silica gel (Method 3630), gel permeation chromatography (Method 3640), and sulfur (Method 3660).	Removed	These techniques are not employed at this lab.
3.4	Added	Please see the glossary in TestAmerica Dayton's Quality Assurance Manual (Document number DT-QAM-001) for definitions.	Consistency with other SOP formats
4.5	Method 3630 (silica gel), Method 3620 (Florisil), or Method 3610 (alumina) are recommended for elimination of the co-elutors.	removed	These techniques are not used at this lab
4.8	n/a	Added technical guidance for reporting	Corporate Technical Memo
5.0	NA	New Safety statements were added by EH&S Director	Comply with new statement
7.4	added	Prepare as indicated in cited tables by adding amounts of standards to a partially filled volumetric flask and then bringing to final volume with appropriate solvent.	Clarification of procedure
7.5	The ICV is prepared from the same	The ICV may be prepared from the same	Indicate that this is not a requirement

Item	Change from	Change to	Reason
8.1	Paragraph format Prep hold time 7 days for waters, 14 days for soils, analysis hold time 40 days	Table format Prep and analytical hold times one year	Consistency with other SOP formats 40 CFR parts 122, 136 et al, Part III- 3/12/2007. Table III
8.1	Added	For concrete and other unusual matrices, the samples may be collected in plastic bottles, plastic bags or other containers.	Clarify procedure for unusual matrices
9.1	Paragraph format	Table format	Consistency with other SOP formats
9.2, 9.3, 9.4, 9.5, 9.6	Moved to section 10		Consistency with other SOP formats
9.3	Laboratory Control Standard (LCS) – A LCS is extracted with extraction batch. The LCS spike is from a different source than the calibration standards.	Laboratory Control Standard (LCS) – A LCS is extracted with each extraction batch. Removed	
9.4	The MS/MSD must meet the same accuracy or recovery criteria outlined in the QA Manual.	Removed	Criteria is maintained in LIMS
9.5	**Surrogates** – All samples and standards will be spiked with two surrogates. For PCBs, only the surrogate DCB will be evaluated.	**Surrogates** – All samples and standards are spiked with two surrogates. For PCBs, only the surrogate DCB is evaluated, unless there is an interference with the DCB. If there is a chromatographic interference with the DCB, then the TCX may be reported in its place.	Provide optional surrogate reporting if chromatographic interference is noted.
9.5.2	…Once the problem has been identified and addressed, corrective action may include the reanalysis of samples, or the extraction and analysis of new sample aliquots	… Once the problem has been identified and addressed, corrective action must include the reanalysis of samples, the extraction and analysis of new sample aliquots or qualification of data if corrective action can not be	

Item	Change from	Change to	Reason
		performed due to lack of sample, hold time exceedence or other issues.	
10.1.1	Method 3610 (alumina) may be used to remove phthalate esters. Method 3620 (Florisil) may be used to separate organochlorine pesticides from aliphatic compounds, aromatics, and nitrogen-containing compounds Method 3630 (silica gel) may be used to separate single component organochlorine pesticides from some interferents.	Removed	These techniques are not in use at this lab
10.5.1	Added	See 10.5.1	Define corrective action for ICV
10.7.6 bullet 3	Added	For OVAP, always report the higher value, qualification of results for >40% RPD is not required.	
Sections 13 & 14	Section 13	Previous section 13 was split into two sections.	For consistency with other SOPs.
Section 15	N/A	DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton. DT-QA-005 Procedure for Balance Calibration Check. DT-QA-006 Thermometer Calibration. DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.	NELAC (PA 2009 audit) requires the reference of these ancillary SOPs.
Section 19	N/A	Move information regarding OVAP from section 19 to references Section 15.	For consistency with other SOPs. Section 19 is not present in non-VAP sops.

Table 1. Example Reporting Limits

Analyte	**Chemical Abstract Service Registry Number**	**Aqueous RL**	**Non-Aqueous RL**
		(µg/L)	**(mg/Kg)**
Aroclor 1016	12674-11-2	0.20 µg/L	0.1 mg/Kg
Aroclor 1221	11104-28-2	0.20 µg/L	0.1 mg/Kg
Aroclor 1232	11141-16-5	0.20 µg/L	0.1 mg/Kg
Aroclor 1242	53469-21-9	0.20 µg/L	0.1 mg/Kg
Aroclor 1248	12672-29-6	0.20 µg/L	0.1 mg/Kg
Aroclor 1254	11097-69-1	0.20 µg/L	0.1 mg/Kg
Aroclor 1260	11096-82-5	0.20 µg/L	0.1 mg/Kg

Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory-specific, method detection limit (MDL) data, project specific DQOs, regulatory requirements are all taken into account, as well as instrument-to-instrument repeatability.

Table 2. PCB Standard Sources (purchased)

	Calibration Standards			*Second Source Standards*		
Analyte	**Vendor/ Catalog #**	**Conc. (µg/mL)**	**Solvent**	**Vendor/ Catalog #**	**Conc. (µg/mL)**	**Solvent**
Aroclor 1016	R-32006	1000	Hexane	S-90123	100	Hexane
Aroclor 1221	R-32007	1000	Hexane	S-90124	100	Hexane
Aroclor 1232	R-32008	1000	Hexane	S-90125	100	Hexane
Aroclor 1242	R-32009	1000	Hexane	S-90126	100	Hexane
Aroclor 1248	R-32010	1000	Hexane	S-90127	100	Hexane
Aroclor 1254	R-32011	1000	Hexane	S-90128	100	Hexane
Aroclor 1260	R-32012	1000	Hexane	S-90129	100	Hexane
Surrogates:						
Decachlorobiphenyl	R-32000	200	Acetone	S-4-8460	200	Isooctane
Tetrachloro-m-xylene	R-32000	200	Acetone	S-4-8460	200	Isooctane

S=Supelco, R=Restek

Standard Vendors and concentrations may change due to lack of availability or other factors. If changes are made then appropriate adjustments to the use and preparation of standards must be evaluated.

Table 3. Calibration Standards

Standard Concentrations		Amount of Stock used			
Cal Standard (ug/L)	**Surr (ug/L)**	**1000 ug/mL Cal Stock 1016 (uL)**	**1000 ug/mL Cal Stock 1260 (uL)**	**200 ug/mL Surr (uL)**	**Final Volume in Hexane**
CAL 1 (20)	4	2	2	2	100 mL
CAL 2 (50)	10	5	5	5	
CAL 3 (100)- CCV	15	10	10	10	
CAL 4 (150)	20	15	15	15	
CAL 5 (200)	40	20	20	20	
ICV*	15	100	100	10	

***Note:** ICV is prepared from a second source, separate from the calibration standards

Calibration levels and concentrations may be changed, however a minimum of 5 standards must be maintained and the low standard must be at or below the RL.

Table 4. Preparation of Single-Point Calibration Standards

Aroclor	Standard Conc. (µg/L)	Surrogate Conc. (µg/L)	Cal. Stock (1000 µg /mL) in 50 mL(µL)	Surr. Stock(200 µg /mL) in 50 mL(µL)
Ar 1221	100	15	5	5
Ar 1232	100	15	5	5
Ar 1242	100	15	5	5
Ar 1248	100	15	5	5
Ar 1254	100	15	5	5

- **Note: ICV is prepared from a second source, separate from the calibration standards.**

Table 5. Recommended Operating Conditions

Using Rtx-CLPesticides/Rtx-CLPesticides2 Columns

Carrier gas	Hydrogen
Carrier gas flow rate	17 cm/sec
Makeup gas	Nitrogen)
Makeup gas flow rate	70 cm/sec
Injector temperature	200 ^{o}C
Detector temperature	300 ^{o}C
Initial temperature	120 ^{o}C
Initial time	0 min
Temperature program	120 ^{o}C to 200 ^{o}C @30 ^{o}/min, 200 to 240 ^{o}C @ 10 ^{o}C/min, 240 to 290 ^{o} C @ 40 ^{o}C/min, Hold at 290 ^{o}C for 5 min.
Final temperature	200 ^{o}C
Injection volume	1 µL

EPC:

Constant Flow	On
Constant Flow Pressure	6 psi
Initial Pressure	7.5 psi
Purge Valve On Time	0.5 min

Title: ICP Total Metals Sample Preparation (aqueous)

SW-846 Method 3010A

Approvals (Signature/Date):

Keith Hutchison 8/29/11 Keith Hutchison Date Department Manager	Jason M. Lykins 8/24/11 Jason Lykins Date EH&S Officer
Violet Fanning 8/29/11 Violet Fanning Date Quality Assurance Manager	Tara Schlenker 8/29/11 Tara Schlenker Date Laboratory Director

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1.0 Scope and Application

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis by inductively coupled argon plasma spectrometry (ICP).

1.2 See Table 2 for elements that may be digested using this procedure.

- Additional elements may be prepared using this procedure, provided all appropriate QC measures are evaluated and found acceptable.
- For OVAP, only compounds listed in the method may be reported using this procedure.

1.3 Current default reporting limits are in the Laboratory Information Management System (LIMS). Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory specific method detection limit (MDL) data, project specific Data Quality Objectives (DQOs) and regulatory requirements are all taken into account.

1.4 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in the Quality Assurance Manual. **OVAP does not allow modifications to the SOP.**

1.5 OVAP does not regulate the preparation or analysis of TCLP samples.

2.0 Summary of Method

An aliquot of well-mixed, homogeneous aqueous sample is accurately measured for sample processing. For total metals analysis of an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is poured up to volume, mixed and allowed to settle prior to analysis. If the sample goes to dryness, it must be discarded and the sample reprepared.

3.0 Definitions

3.1 Total Recoverable - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

3.2 Total - The concentration determined on an unfiltered sample following vigorous digestion.

3.3 Element - The Laboratory Information Management System.

3.4 Please see the Glossary in the Quality Assurance Manual, DT-QAM-001, for additional definitions.

4.0 Interferences

4.1 Interferences are discussed in the referring analytical methods.

4.2 Boron and silica from the glassware will leach into the sample solution during and following sample processing, therefore, PTFE plastic labware is used.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual (CW-E-M-001) 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

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

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 standards 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
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

- Hot Block / Hot Plate capable of maintaining temperatures of $95^{o} \pm 5°C$.
- Environmental Express Disposable Digestion Cups - 50 mL with caps (the manufacturer Volume Certification for each lot is kept on file).
- Sample tubes, hinged caps, 70 mL labware is verified internally if used for volumetric purposes and not accompanied by a certificate
- Macropipettes and micropipettes with disposable tips.
- Miscellaneous laboratory glassware and disposable plastic ware.
- Filter paper – Whatman No. 4 or equivalent.
- Thermometer that has been calibrated against a NIST thermometer.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents 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 questionable, analyze the reagent to determine the level of impurities.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

All standards/reagents are stored at room temperature.

7.1 **Reagent Water**. Reagent water is interference free. All references to water in this SOP refer to reagent water unless otherwise specified. The Metals Department uses Deionized Water as Reagent Water.

7.2 **Nitric Acid (HNO_3), Concentrated:** Trace Metal grade or better. Shelf life is one year after opening or manufacturer's expiration date (whichever is shorter).

7.3 **Hydrochloric Acid (HCl), Concentrated:** Trace Metal grade or better. Self life is one year after opening or manufacturer's expiration date (whichever is shorter).

7.4 **LCS/MS/MSD Spike 1:** Quality Control Standard 7 from Spex (1,000 mg/L of K; 100 mg/L of Ag, Al, B, Ba, Na; 50 mg/L of Si).

7.5 **LCS/MS/MSD Spike 2:** Quality Control Standard 21 from Spex (100 mg/L of As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn).

7.6 **LCS/MS/MSD Spike 3:** Alt. Metals III Standard from Spex or Environmental Express (500 mg/L of Ca and Na; 100 mg/L of K and Mg).

7.7 **LCS/MS/MSD Spike 4:** Multi Element (ME) Spike Standard (100 mg/L of Si, Sr, Sn, and Tl). Into a 500 mL volumetric, add the following:

7.7.1 Approximately 50 mL of Deionized Water.
7.7.2 30 mL of Concentrated nitric acid (HNO_3).
7.7.3 25 mL of Concentrated hydrochloric acid (HCl).
7.7.4 5 mL of 10,000 mg/L Si Standard.
7.7.5 5 mL of 10,000 mg/L Sr Standard.
7.7.6 5 mL of 10,000 mg/L Sn Standard.
7.7.7 5 mL of 10,000 mg/L Tl Standard.
7.7.8 Dilute to 500 mL mark and mix well.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

OVAP and most other environmental samples require compliance with the information detailed in the analytical methods.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	Plastic or glass	250 mL	pH <2 with HNO3, chill to <6.0°C but not frozen	180 days from sampling to analysis	40 CFR Part 136

8.2 All aqueous metals samples (except Cr VI) must be acidified to a pH <2 with nitric acid upon collection. Samples are collected in pre-preserved sample containers. Proper preservation (pH <2) is checked prior to digestion.

8.2.1 Document preservation check. This may be done in LIMs or on a benchsheet. pH is additionally noted on the sample bottle cap by a red or black line.

8.2.2 If samples are found to be pH >2, then additional acid is added. Document amount and lot number of acid as well as date and time acid is added. Hold samples for at least 24 hours after preservation and recheck pH. If pH is now <2, proceed with sample prep. If pH is >2, then acid is added until pH holds at <2 after 24 hours. Any sample preserved at the lab is flagged like “P27 - The sample, as received, was not preserved in accordance with the referenced analytical method, but was preserved by the laboratory”.

8.3 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus, which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption, thus the collection and treatment of the sample prior to analysis requires particular attention. The quality control program must document through the use of spikes sample, reagent and sample blanks, that cleaning procedures are adequate. Care must be taken to verify the fact that the containers in which acid digested samples, blanks, and standards are packaged do not contribute contaminants.

8.4 Before collection of the sample, a decision must be made as to the type of data desired, i.e., dissolved, suspended, or total.

9.0 Quality Control

9.1 The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency
Method Blank (MB)	1 per preparation batch[1]
Laboratory Control Sample (LCS)	1 per preparation batch[1]
Matrix Spike/Matrix Spike Duplicate (MS/MSD)[2]	1 per preparation batch[1]
Duplicate (DUP)[2]- Post Digestion Dilution Test	1 per preparation batch[1]
Post Spike [2]	1 per preparation batch[1]

[1]Preparation batch is limited to 20 samples
[2]The sample selection for MS/MSD/DUP and Post Spike is random, unless specifically requested by a client.

9.2 **Batching samples using ELEMENT**

9.2.1 One / Method Blank (MB). This is automatically added by ELEMENT. This MB is an aliquot of Deionized water that is carried through the digestion procedure and contains the same volumes of reagents as the sample solutions. The MB is useful in determining if samples are being contaminated from the reagents or environment.

9.2.2 One Laboratory Control Sample (LCS) This is automatically added by ELEMENT. The LCS/ is an aliquot of Deionized water that is spiked with a known concentration of metals and is carried through the same procedure as a sample would go through. The LCS is useful in determining accuracy by showing that a know concentration of metals can be taken through the procedure and recovered within the established acceptance limits.

9.2.3 One Matrix Spike (MS) / Matrix Spike Duplicate (MSD) pair. This is automatically added by ELEMENT; however, the digestion technician must select which sample to use for this pre-digestion spike requirement. This selected sample is digested three times: once non-spiked, once spiked as the MS, and once spiked as the MSD. The MS/MSD is spiked with a know concentration of metals. The MS/MSD is useful in determining precision and bias.

9.2.4 One Duplicate (DUP) to be designated as a Post-Digestion Dilution (1+4) Test Sample. This is automatically added by ELEMENT; however, the instrumentation analyst selects which sample to use for this post-digestion procedure and adds a data qualification flag to indicate that it is a Post-Digestion Dilution (1+4) Test Sample rather than a duplicate digested sample.

9.2.5 One Post Spike (PS) to be designated as a Post-Digestion Spike sample. This is automatically added by ELEMENT; however, the instrumentation analyst selects which sample to use for this post-digestion procedure as well as documents the appropriate spike solutions and amounts to be added

9.3 Please see the analytical procedure SOP for acceptance criteria and corrective actions.

10.0 Procedure

Note: Before pouring up samples, rinse each digestion vessel three times with DI water.

10.1 Pour up 25 mL of sample into an approved digestion vessel.

Note: Sample volumes can be changed provided the volumes of reagents/standards used are adjusted proportionally.

- For the Method Blank (MB) and the Laboratory Control Sample (LCS), add 25 mL of Deionized water.

10.2 To the Laboratory Control Sample (LCS) and to the Matrix Spike (MS) and Matrix Spike Duplicate (MSD) vessels, add the following:

- 0.250 mL of Spike 1 (Quality Control Standard 7 from Spex)
- 0.250 mL of Spike 2 (Quality Control Standard 21 from Spex)
- 1.0 mL of Spike 3 (Alt. Metals III from Spex or Environmental Express)
- 1.0 mL of Spike 4 (Multi Element "ME" Standard)

10.3 Add 0.75 mL of Concentrated HNO_3

10.4 In the Hot Block, evaporate samples to a low volume (about 5-7 mLs). Do not boil or allow samples to go dry.

Note: All steps requiring the use of acids must be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment.

10.5 Add a reflux cap to the digestion vessel and add an additional 0.75 mL of Concentrated HNO_3. reflux (approximately 30 minutes).

Note: If necessary add additional acid, HN03, until digestate is light in color or does not change.

10.6 If additional acid is added take samples to a low volume (about 5-7 mL).

10.7 Add 1.25 mL of conc HCl and reflux for an additional 15 minutes to dissolve any precipitate or residue. Wash down sides of digestion vessel with DI water while bringing up to a final volume of 25 mL. Mix well.

10.8 Let sample settle prior to analysis. At the discretion and preference of the instrumentation analysts, particulates in the digestate can then be removed by filtration, by centrifugation, or by allowing the sample to settle.

Note: A hot plate capable of maintaining temperatures of 90° to 95° C may be used in place of the Hot Block.

10.9 In ELEMENT, be sure to properly document the block ID, source and the amount of all standards, acids, and reagents used; the initial and final volumes of each sample; the temperature reading from the maximum registering thermometer; and the date & time the digestion procedure was performed.

10.10 **Procedure for TCLP**

10.10.1 When TCLP leachates are received from the leaching group, pour off approx. 50mL of an unpreserved TCLP leachate into a separate container and designate as MS/MSD. Preserve remaining TCLP leachate (s) with approx. 2mL of HNO3 and check that pH is <2 within 30min of being received. This pour off is performed to facilitate the spiking of the MS/MSD prior to preservation.

Note: Sample volumes can be changed provided the volumes of reagents/standards used are adjusted proportionally.

10.10.2 Pour up 10 mL of unpreserved TCLP leachate into an approved digestion vessel.

10.10.3 For the Method Blank (MB) and the Laboratory Control Sample (LCS, add 10 mL of Deionized water.

10.10.4 For the Matrix Spike (MS) and Matrix Spike Duplicate (MSD) add 10mL of unpreserved TCLP leachate

10.10.5 To the Laboratory Control Sample (LCS and to the Matrix Spike (MS) and Matrix

Spike Duplicate (MSD) vessels, add the following:

- 0.50 mL of Spike 1 (Quality Control Standard 7 from Spex)
- 0.50 mL of Spike 2 (Quality Control Standard 21 from Spex)
- 2.0 mL of Spike 3 (Alt. Metals III from Spex or Environmental Express
- 2.0 mL of Spike 4 (Multi Element "ME" Standard)

10.10.6 Add 1.5 mL of Concentrated HNO_3

10.10.7 In the Hot Block, evaporate samples to a low volume (about 5-7 mLs). Do not boil or allow samples to go dry.

Note: All steps requiring the use of acids must be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment.

10.10.8 Add an additional 1.5 mL of Concentrated HNO_3 and place a reflux cap on the digestion vessel.

10.10.9 Reflux (approximately 30 minutes).

10.10.10 Take samples to a low volume (about 5-7mL).

10.10.11 Add 2.50 mL of conc HCl.

10.10.12 Reflux for an additional 15 minutes to dissolve any precipitate or residue. Wash down sides of digestion vessel with DI water while bringing up to a final volume of 50 mL. Mix well.

10.10.13 Let sample settle prior to analysis. At the discretion and preference of the instrumentation analysts, particulates in the digestate can then be removed by filtration, by centrifugation, or by allowing the sample to settle.

Note: A hot plate capable of maintaining temperatures of $95^{o} \pm 5°C$ may be used in place of the Hot Block.

10.10.14 In ELEMENT, be sure to properly document the block ID, source and the amount of all standards, acids, and reagents used; the initial and final volumes of each sample; the temperature reading from the maximum registering thermometer; and the date & time the digestion procedure was performed.

11.0 Calculations / Data Reduction - None Applicable.

12.0 Method Performance

The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.1 Demonstration of Capabilities – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.2 Method Detection Limit Study – A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

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 accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.1 The following waste streams are produced when this method is carried out:

- Acidic waste containing nitric & hydrochloric acids is neutralized and discharged into the sanitary sewer.
- Contaminated disposable materials utilized for the analysis is disposed of in the general trash.

15.0 References / Cross-References

15.1 Inductively Coupled Plasma – Atomic Emission Spectrometric Method for Trace Metal Analysis of Water and Wastes Method 200.7, 40 CFR 136 Appendix C, 7/1/1999 Edition

15.2 SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", 3rd Edition, Method referenced 3010A.

15.3 DT-QA-006 Thermometer Calibration

15.4 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.

15.5 This is an OVAP approved SOP. All changes must be approved by OVAP prior to implementation.

16.0 Method Modifications:

Item	Method	Modification
9.4	EPA 200.7	Use of Heating Block instead of Hot Plate
9.4	EPA 200.7	Use of 50 mL disposable digestion tubes instead of Griffin beakers
1.2	SW-3010A	Also may prepare Li, Si, Ag, Sb, B, Sr, Sn and Ti by this procedure.
7.1	SW-3010A	A ribbed watch glass is not initially used, as this would prevent the necessary volume reduction.
7.1	SW-3010A	Additional Concentrated HNO_3 acid is used.
7.1	SW-3010A	Use 25 ml instead of 100 ml and 0.75 ml of conc. HNO3 instead of 3 ml of conc. HN03. The percent HNO3 remains the same at 3%.
7.0	SW-3010A	Do not remove from heat and allow to cool before adding the second volume of Nitric acid HNO3
7.2	SW-3010A	Do not remove from heat and allow to cool before adding the hydrochloric acid, HCL.

17.0 Attachments

Table 1 Example Preparation of Solutions
Table 2 Example Concentration of LCS, MS, MSD
Table 3 TCLP prep outline
Table 4 Aqueous prep outline

18.0 Revision History

18.1 Revision Dates

- 9/01/11 Biennial review
- 4/15/2009 replaces 8/23/2007

18.2 Changes from last revision

Section	Change from	Change to	Reason
1.2	Added	Additional elements may be prepared using this procedure, providedall appropriate QC measures are evaluated and found acceptable.	Clarification, consistency with other SOPs
1.3	Added	See text in SOP	SOP review checklist requirement
1.5	Added	See text in SOP	VAP regulatory clarification
3.4	Added	See text in SOP	SOP review checklist requirement
6	Maximum registering thermometer.	Thermometer that has been calibrated against a NIST thermometer.	Change in equipment
Entire SOP	Removed	BS, Blank Spike	Improve naming convention consistency
8.1	Added	OVAP and most other environmental samples require compliance with the information detailed in the analytical methods.	VAP regulatory clarification
8.2	Removed	…or as soon as received at the lab…	Checks not performed upon receipt
8.2.1	Added	Document preservation check. This may be done in LIMs or on a benchsheet. pH is additionally notedon the sample bottle cap by a red or black line.	2011 corporate audit
8.2.2	Added	Document amount and lot number of acid as well as date and time acid is added. Hold samples for at least 24 hours after preservation and recheck pH. If pH is now <2, proceed with sample prep. If pH is >2, then acid is added until pH holds at <2 after 24 hours.	2011 corporate audit

Section	Change from	Change to	Reason
8.2.2	Removed	If the sample pH >2 the time the additional acid is added is indicated on the sample bottle cap and the amount of acid and acid lot number is recorded on the bottle cap. From the time written on the sample bottle cap the 24 hour wait time can be determined before the pH is checked again. The sample must be held for at least 24 hours after preservation.	2011 corporate audit
8.2.2	Added	Any sample preserved at the lab is flagged like "P27 – The sample, as received, was not preserved in accordance with the referenced analytical method, but was preserved by the laboratory."	2011 corporate audit
Entire SOP	Removed	PB, Blk, Preparation Blank	Improve naming convention consistency
9.3	Added	See text in SOP	Clarify corrective action procedure
10.4 & 10.8	Removed "near dryness"	Changed to "a low volume"	Clarification of procedure
10.5 & 10.8	Removed the statement "removed from heat and allowed to cool" and "Place back in the hot bock and'	Removed statements	Clarification of procedure
10.1	Added	document the block ID	Clarify requirements
10.11	No Procedure for TCLP preparation was stated	Included a section for the preparation of TCLP leachates	Up date preparation procedure
14	Added	in accordance with all federal and state laws and regulations.	Clarification and consistency with other SOPs
15.3, 15.4, 15.5	Added	See text in SOP	Provide reference for ancillary equipment and procedures
16	Added	Use 25 ml instead of 100 ml and 0.75 ml of conc. HNO3 instead of 3 ml of conc. HN03. The percent HNO3 remains the same at 3%.	Update method modifications
16	Added	Do no remove from heat and allow to cool before adding the second volume of Nitric acid HNO3	Update method modifications
16	Added	Do not remove from heat and allow to cool before adding the hydrochloric acid, HCL.	Update method modifications

Table 1 Example Preparation of Solutions

Standard	Volume	Solution ID	Diluted to
LCS (aqueous)	0.25 mL 0.25 mL 1.0 mL 1.0 mL	QC-7 QC-21 Alt. Metals III ME Spike	25 mL of DI water
MS	0.25 mL 0.25 mL 1.0 mL 1.0 mL	QC-7 QC-21 Alt. Metals III ME Spike	25 mL of Sample
MSD	0.25 mL 0.25 mL 1.0 mL 1.0 mL	QC-7 QC-21 Alt. Metals III ME Spike	25 mL of Sample

Table 2 Example Concentration of LCS, MS, MSD

Digested LCS/MS/MSD Concentration (after the addition of the standards)

Element	mg/L
Aluminum	1.00
Antimony	1.00
Arsenic	1.00
Barium	1.00
Beryllium	1.00
Boron	1.00
Calcium	21.0
Cadmium	1.00
Chromium	1.00
Cobalt	1.00
Copper	1.00
Iron	1.00
Lead	1.00
Lithium	1.00
Magnesium	5.00
Manganese	1.00
Molybdenum	1.00
Nickel	1.00
Potassium	14.0
Selenium	1.00
Silicon	4.5
Silver	1.00
Sodium	21.0
Strontium	5.00
Thallium	1.00
Tin	4.0
Titanium	1.00
Vanadium	1.00
Zinc	1.00

Table 3 – ICP TCLP Metals Prep SW 3010A outline (may be posted in laboratory as a separate sheet)

This outline does not replace the SOP. Use of this outline is restricted to analysts who have read, and been approved to conduct procedures as described in, the affiliated SOP.

1.0 Pour off approx 50mL of unpreserved TCLP leachate and designate as MS/MSD. This pour off is performed to facilitate the spiking of the MS/MSD prior to preservation.

2.0 Within 30 minutes of receipt, preserve remaining leachate with approx 2mL of Nitric and check that pH is <2

3.0 Use green screw cap containers, Environmental Express part SC475 or EE SC475

4.0 Rinse all containers 3 times with DI water

5.0 Pour samples up to 10mL, 10 ml DI water for the BLK and BS1

6.0 For MS/MSD use 10mL of unpreserved leachate

- 0.50mL of Spike 7 in BS, MS, MSD (500uL)
- 0.50mL of Spike 21 in BS, MS, MSD (500uL)
- 2.0mL of Alt. Metals 3 in BS, MS, MSD
- 2.0mL of Spike 4 in BS, MS, MSD

7.0 Add 1.50mL of concentrated Nitric acid to each sample

8.0 Cook down to ~5 – 7 mL

9.0 Place disposable reflux cap on each sample

10.0 Add 1.50mL of concentrated Nitric acid to each sample

11.0 Wait 30 minutes

12.0 Add 2.50mL of Hydrochloric acid to each sample through reflux cap

13.0 Wait 15 minutes

14.0 Take samples off hot block

15.0 Let samples cool ~15 minutes

16.0 Remove reflux caps and throw away

17.0 Fill each sample up to 50mL with DI water

18.0 Re-Label

19.0 Take to ICP analyst

Title: ICP Non-Aqueous Sample Preparation

SW-846 Method 3050B

Approvals (Signature/Date):

9/15/11 Keith Hutchison Department Manager	9/02/11 Jason Lykins EH&S Officer
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1.0 Scope and Application

1.1 This method is for the preparation of sediments, sludges, and soil samples for analysis by ICP.

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available". By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment.

1.3 Please see Table 1 for a list of elements that may be digested by this procedure.

- Additional elements may be prepared using this procedure, provided all appropriate QC measures are evaluated and found acceptable.
- For OVAP, only compounds listed in the method may be reported using this procedure.

1.4 Current default reporting limits are in the Laboratory Information Management System (LIMS). Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory specific method detection limit (MDL) data, project specific Data Quality Objectives (DQOs) and regulatory requirements are all taken into account.

1.5 On occasion clients may request slight modifications to this SOP. These modifications are handled following the procedures outlined in the Quality Assurance Manual. **OVAP does not allow modifications to the SOP.**

2.0 Summary of Method

2.1 For the digestion of samples, a representative 1.5 gram sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). If lower reporting limits are required up to a 5 g sample may be used. Additional nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) may be required with the higher weight of sample.

2.2 The resultant digestate is reduced in volume while heating and then diluted to a final volume of 50 mL.

2.3 Hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed in order to stabilize silver and antimony.

2.4 If required, a separate sample aliquot must be dried for a total percent solids determination.

3.0 Definitions

3.1 Element- The Laboratory Information Management System.

3.2 Please see the Glossary in the Quality Assurance Manual, DT-QAM-001, for additional definitions.

4.0 Interferences

4.1 Interferences are discussed in the referring analytical methods.

4.2 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material must be processed in accordance with the Quality Control Section.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual (CW-E-M-001) 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

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

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 standards 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
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

- Hot Block / Hot Plate capable of maintaining temperature of 95° C +/- 5° C.
- Environmental Express Disposable screw cap Digestion Cups (part Number SC475) – 50 mL with caps (the manufacturer volume Certification for each lot is kept on file).
- Sample tubes, hinged caps, 70 mL or 100 ml Note: the 100 ml hinge cap tubes are not used for final volume determination.
- Macropipettes and micropipettes with disposable tips.
- Miscellaneous laboratory glassware and disposable plastic ware: All glassware and disposable plastic ware must be rinsed three times with deionized water before sample preparation.
- Top loader balance capable of weighing to the nearest 0.01 gram. Analytical balance capable of weighing to the nearest 0.1 mg may be used when measuring very limited volume samples (such as paint chips and paint scrapings).
- Centrifuge and centrifuge tubes.
- Thermometer that has been calibrated against a NIST thermometer.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

Reagent grade chemicals must 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 questionable, analyze the reagent to determine the level of impurities.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

All standards/reagents are stored at room temperature.

7.1 **Reagent Water**. Reagent water is interference free. All references to water in this SOP refer to reagent water unless otherwise specified. The Metals Department uses Deionized Water as Reagent Water.

7.2 **Nitric Acid (HNO_3), Concentrated:** Trace Metal grade or better. Shelf life is one year after opening or manufacturer's expiration date (whichever is shorter).

7.3 **Hydrochloric Acid (HCl), Concentrated:** Trace Metal grade or better. Shelf life is one year after opening or manufacturer's expiration date (whichever is shorter).

7.4 **Hydrogen peroxide (30%):** H_2O_2, Shelf life is one year after opening or manufacture's expiration date (whichever is shorter).

7.5 **Quality control Standards 21 from Spex:** (100 mg/L of As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn). Shelf life is one year after opening or manufacturer's expiration (whichever is shorter)

7.6 **Quality control Standards 7 from Spex:** (1,000 mg/L of K; 100 mg/L of Ag, Al, B, Ba, Na; 50 mg/L of Si). Shelf life is one year after opening or manufacturer's expiration (whichever is shorter)

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

8.2 OVAP and most other environmental samples require compliance with the information detailed in the analytical methods.

Matrix	Sample Container *	Min. Sample Size	Preservation	Holding Time	Reference
Non-Aqueous	Plastic or glass	200 g	<6.0°C but not frozen.	180 days from sampling to analysis	40 CFR Part 136

8.3 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus, which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorbtion and (b) by depleting concentrations through adsorption, thus the collection and treatment of the sample prior to analysis requires particular attention. The quality control program must document through the use of spikes sample, reagent and sample blanks, that cleaning procedures are adequate. Care must be taken to verity the fact that the containers in which acid digested samples, blanks, and standards are packaged do not contribute contaminants.

*For concrete and other unusual matrices, the samples may be collected in plastic bottles, plastic bags or other containers.

9.0 Quality Control

9.1 The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency
Method Blank (MB)	1 per preparation batch[1]
Laboratory Control Sample (LCS)	1 per preparation batch[1]
Matrix Spike/Matrix Spike Duplicate (MS/MSD)[2]	1 per preparation batch[1]
Duplicate (DUP)[2]- Post Digestion Dilution Test	1 per preparation batch[1]
Post Spike [2]	1 per preparation batch[1]

[1]Preparation batch is limited to 20 samples
[2]The sample selection for MS/MSD/DUP and Post Spike is random, unless specifically requested by a client.

9.2 **Batching samples using ELEMENT**

9.2.1 One / Method Blank (MB). This is automatically added by ELEMENT. This MB is an aliquot of Deionized water that is carried through the digestion procedure and contains the same volumes of reagents as the sample solutions. Clean PTFE boiling chips are added to approximate the amount or weight of a sample to represent a non aqueous substance in the blank. The MB is useful in determining if samples are being contaminated from the reagents or environment.

9.2.2 One Laboratory Control Sample (LCS) This is automatically added by ELEMENT. The LCS/ is an aliquot of Deionized water that is spiked with a known concentration of metals and is carried through the same procedure as a sample would go through. , (same volumes of reagents). Clean PTFE boiling chips are added to approximate the amount or weight of a sample to represent a non aqueous substance in the LCS. The LCS is useful in determining accuracy by showing that a know concentration of metals can be taken through the procedure and recovered within the established acceptance limits.

9.2.3 One Matrix Spike (MS) / Matrix Spike Duplicate (MSD) pair. This is automatically added by ELEMENT; however, the digestion technician must select which sample to use for this pre-digestion spike requirement. This selected sample is digested three times: once non-spiked, once spiked as the MS, and once spiked as the MSD. The MS/MSD is spiked with a known concentration of metals. The MS/MSD is useful in determining precision and bias.

9.2.4 One Duplicate (DUP) to be designated as a Post-Digestion Dilution (1+4) Test Sample. This is automatically added by ELEMENT; however the preparations analyst must remove the DUP from the batch before saving. The instrumentation analyst must add the Duplicate back to the batch and select which sample to use for this post-digestion procedure and add a data qualification flag to indicate that it is a Post-Digestion Dilution (1+4) Test Sample rather than a duplicate digested sample.

9.2.5 One Post Spike (PS) to be designated as a Post-Digestion Spike sample. This is automatically added by ELEMENT; however the preparations analyst must remove the PS from the batch before saving. The instrumentation analyst must add the PS back to the back to the batch and selects which sample to use for this post-digestion procedure as well as document the appropriate spike solutions and amounts to be added.

9.3 Please see the analytical procedure SOP for acceptance criteria and corrective actions.

10.0 Procedure

10.1 All labware should be rinsed three times with deionized water before use in sample digestion. (70 mL plastic flip tops (SC601) and the 50 mL green screw cap digestion cups (SC475)

10.2 Mix the sample thoroughly to achieve homogeneity. If appropriate and necessary, a USS #10 sieve may be used. All equipment used for homogenization must be cleaned prior to use to minimize the potential of cross-contamination.

NOTE: All steps requiring the use of acids must be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment.

10.3 Into a 70 mL disposable plastic digestion vessel with a flip top lid, transfer a 1.5 – 1.59 g sample weighed to the nearest 0.01 g. For samples with high liquid content or that need a lower reporting limit, a larger sample size (usually 5.0 g) may be used as long as digestion is completed. For samples with limited amount and/or weights less than 0.5g use an Analytical Balance to weigh the sample. Record the weight to 0.001g.

10.4 For the Method Blank (MB) and the Laboratory Control Sample (LCS) use approximately 5 mL of DI water and enough clean PTFE boiling chips to approximate the weight of sample used..

10.5 Add 5 mL of Deionized Water to all samples and MS/MSD.

10.6 To the Laboratory Control Sample (LCS) and to the Matrix Spike (MS) Matrix Spike Duplicate (MSD) vessels add, using a macropipetter:

- 0.5 mL of Quality Control Standard 21 from Spex
- 0.5 mL of Quality Control Standads 7 from Spex

10.7 Add 5 ml of Concentrated HNO_3, (use a macropipetter or bottle top dispenser) mix the slurry, and cover the vessel loosely with the flip top lid.

10.8 Heat the sample to 95°C $\pm$ 5°C and reflux for 10 -15 minutes without boiling.

10.9 While still in the hot block add 5 mL of concentrated HNO_3 (use a macropipetter or bottle top dispenser), cover the vessel loosely with the flip top lid and reflex for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of conc. HNO_3) repeatedly until no brown fumes are given off by the sample indicating the complete reaction with HNO_3.

10.10 Continue to cover the vessel loosely with the flip top lid and either allow the solution to evaporate to approximately 10 mL without boiling or heat at 95°C $\pm$ 5°C without boiling for one and a half to two hours. <u>Maintain a covering of solution over the bottom of the vessel at all times.</u>

10.11 While still in the hot block dd 3 mL of 30% H_2O_2. Using a new large disposable pipetter for each addition of H_2O_2 and for each sample Cover the vessel loosely with the flip top lid and proceed with 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.

10.12 Continue to add 30% H_2O_2 dropwise using a new disposable pipette for each addition of H_2O_2 and for each sample, while warming until the effervescence is minimal or until the general sample appearance is unchanged.

<u>NOTE</u>: Do not add more than a total of 10 mL 30% H_2O_2.

10.13 Cover the vessel loosely with the flip top lid and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 10 mL or heat at 95°C $\pm$ 5°C without boiling for 30 – 45 min.. Maintain a covering of solution over the bottom of the vessel at all times.

10.14 While still in the hot block, add 10 mL of concentrated HCl - use a macropipetter or bottle top dispenser, to the sample digestate, cover the vessel loosely with the flip top lid, and reflux for 15 minutes. Remove from hot plate

10.15 After cooling, transfer the contents of the 70mL digestion vessel into a 50mL Environmental Express Disposable Digestion cup (SC475). Rinse the digestion vessel at least three times with a small amount of deionized water. Dilute to 50 mL with deionized water and mix well. At the discretion and preference of the instrumentation analysts,

particulates in the digestate can then be removed by filtration, by centrifugation, or by allowing the sample to settle. The sample is ready for analysis.

10.16 In ELEMENT, under LABORATORY and BATCH, be sure to properly document the source and the amount of all standards, acids and reagents used; the initial weights and final volumes of each sample; the temperature reading from the thermometer , the label of hot block used for digestion and the date & time the digestion procedure was performed.

11.0 Calculations / Data Reduction - None Applicable.

12.0 Method Performance

The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.1 **Demonstration of Capabilities** - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.2 **Method Detection Limit Study** - A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

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 accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.1 The following waste streams are produced when this method is carried out:

14.1.1 Acidic waste containing nitric & hydrochloric acids is neutralized and discharged into the sanitary sewer.

14.1.2 Contaminated disposable materials utilized for the analysis is disposed of in the general trash.

15.0 References / Cross-References

15.1 SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", 3rd Edition, Methods referenced 3050B and 6010B.

15.2 DT-QA-005 Procedure for Balance Calibration Check

15.3 DT-QA-006 Thermometer Calibration

15.4 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.

15.5 This is an OVAP approved SOP. All changes must be approved by OVAP prior to implementation.

16.0 Method Modifications

Modifications:

Item	Method	Modification
7.2	SW-3050B	Instead of adding 10 mL of 1:1 HNO_3, we add 5 mL of Deionized Water and 10 mL of concentrated HNO_3 and heat to 95C +/_ 5°C the sample and reflux for 30 minutes
7.4	SW-3050B	Final sample volume is 50 mL.

17.0 Attachments

Table 1 Elements that may be digested using this procedure.

Table 2 ICP Non Aqueous Prep 3050 outline

18.0 Revision History

18.1 Revision Dates

- 9/28/11 – Biennial review and update
- 6/24/09
- 8/24/07

18.2 Changes from last revision

Section	Change from	Change to	Reason
1.3	Added	Additional elements may be prepared using this procedure, provided all appropriate QC measures are evaluated and found acceptable.	Clarification, consistency with other SOPs
1.4	Added	For OVAP, only compounds listed in the method may be reported using this procedure.	OVAP compliance
1.4	Added	Current default reporting limits are in the Laboratory Information Management System (LIMS). Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory specific method detection limit (MDL) data, project specific Data Quality Objectives (DQOs) and regulatory requirements are all taken into account.	Consistency with other SOPs

Section	Change from	Change to	Reason
3.2	Added	Please see the Glossary in the Quality Assurance Manual, DT-QAM-001, for additional definitions.	Consistency with other SOPs
6	90° to 95°C	95° C +/- 5 ^{o} C.	Clarify requirement
6	Disposable Digestion Cups	Disposable screw cap Digestion Cups (SC475)	Added screw cap and part number (SC475)
6	Added	Thermometer that has been calibrated against a NIST thermometer.	Internal audit finding
7.4, 7.5, 7.6	Added	Shelf life is one year after opening or manufacture's expiration (which ever is shorter)	Internal audit finding
9.2.1	Added	Clean PTFE boiling chips are added to equal the amount or weight of a sample to represent a non aqueous substance in the blank.	Internal audit finding
Entire SOP	Removed	BS, Blank Spike	Improve naming convention consistency
8.1	Added	OVAP and most other environmental samples require compliance with the information detailed in the analytical methods.	OVAP regulatory clarification
9.2.2	Added	Clean PTFE boiling chips are added to equal the amount or weight of a sample to represent a non aqueous substance in the LCS.	Internal audit finding
9.2.4	This is automatically added by ELEMENT; however the instrumentation analyst	the preparations analysis must remove the DUP from the batch before saving. The instrumentation analyst must add the Duplicate back to the batch and selects which sample to use for this post-digestion procedure and adds a data qualification flag to indicate that it is a Post-Digestion Dilution (1+4) Test Sample rather than a duplicate digested sample	Change in procedure
9.2.5	… the instrumentation analyst selects which sample to use for this post-digestion procedure as well as …	… the preparations analyst must remove the PS from the batch before saving. The instrumentation analyst must add the PS back to the back to the batch and selects which sample to use for this post-digestion procedure as well as…	Change in procedure
10.1	Added	All labware should be rensed three time with deionized water before use during sample digestion. (70 ml plastic flip tops (SC601) and the 50 ml green screw digestion cups (SC475).	Internal audit finding
10.3	Added	For samples with limited amount and/or weighs less than 0.5 g the Analytical Balance in the instrumentation lab must be used to weigh the sample, record the weight to 0.001g.	Internal audit finding

Section	Change from	Change to	Reason
Entire SOP	Removed	PB, Blk, Preparation Blank	Improve naming convention consistency
10.4	Added	and enough cleaned PTFE boiling chips to equal the amount or weight of sample used.	Internal audit finding
10.5	Not specified to add 5mlwater to MS/MSD	MS/MSD	Internal audit finding
10.7, 10.9, 10.14	Not specified how to add the reagent	(use a macropipetter or bottle top dispenser),	Clarify procedure
10.9, 10.11, 10.14	Remove from hot block and allow to cool	While still in the hot block	Clarification of instructions
10.11	Not specified how to add the H_2O_2	Using a new large disposable pipette for each addition of H_2O_2 and for each sample	Clarify procedure
10.12	Not specified how to add the H_2O_2	dropwise using a new disposable pipette for each addition of H_2O_2 and for each sample, while	Clarify procedure
10.15	Added	70 mL flip top digestion vessel into an Environmental Express Disposable screw cap Digestion cup part # SC475. Rinse the digestion vessel at least three times with a small amount of deionized water and put the rinse solution into the SC475 screw cap digestion cup with the sample digestate	Clarify procedure

Table 1 Elements that may be digested using this procedure

Aluminum	Lead
Antimony	Magnesium
Arsenic	Manganese
Barium	Molybdenum
Beryllium	Nickel
Boron	Potassium
Cadmium	Selenium
Calcium	Silicon
Chromium	Silver
Cobalt	Sodium
Copper	Thallium
Iron	Vanadium
Tin	Zinc
Titanium	

Table 2 ICP Non Aqueous Prep 3050 outline (may be posted in laboratory as a separate sheet)
This outline <u>does not replace</u> the SOP. Use of this outline is restricted to analysts who have read, and been approved to conduct procedures as described in, the affiliated SOP.

1. Rinse containers three times with deionized water
2. Weigh samples in flip top containers
    a. Samples are usually weighed out to 1.5g
    b. Some samples have specific RLs or have special comments to be weighed out to 5.0g. Paint chips are also special weights of 0.50g.
    c. If not sure, ask Dept Manager or the analyst
3. Add ~5mL DI water to each sample
4. In Blank and BS also add ~5 boiling chips
5. SPIKES:
    - 0.50mL of QC 7 in BS, MS, MSD (500uL)
    - 0.50mL of QC 21 in BS, MS, MSD (500uL)
6. Add 5mL of conc. Nitric acid to each sample
7. Place samples in Mod Block
8. Cook and reflux for 10 to 15 minutes, without boiling
9. Add 5 mL conc Nitric acid
10. Cover loosely and reflux for 30 minutes
11. If brown fumes are generated, repeat additions of 5mL conc Nitric and heat until fumes are no longer given off.
12. Cook down to a little over 10mL (1.5 to 2 hours)

NOTE: Make sure samples do not go below 5mL

13. -Add ~3mL to Hydrogen Peroxide (large disposable pipette is about 3mL when full)

NOTE: Be careful when adding because samples will boil over and possibly contaminate the other samples. Add VERY slowly to every sample or add a couple drops to a couple of samples and switch back and forth.

14. Continue to add 30% Hydrogen Peroxide drop-wise while warming until effervescence is minimal or sample appears unchanged

NOTE: Do not add more than a total of 10mL peroxide

15. Cook samples back down to 10mL (30 – 45 minutes)
16. Add 10 mL of concentrated Hydrochloric acid
17. Reflux 15 minutes
18. Take samples out of Mod Block
19. Let samples cool ~15minutes
20. Pour from large flip top into <u>labeled</u> green screw cap containers
    a. Make sure to rinse flip top container with DI water and pour water into the green screw cap container, making sure to get as much sample out of the flip top as possible.
21. Fill green screw cap containers up to 50mL with DI water
22. Take to ICP analyst

Title: ICP-MS Non-Aqueous Sample Preparation

SW-846 Method 3050B

Approvals (Signature/Date):

8/29/11 Keith Hutchison Date Department Manager	8/30/11 Jason Lykins Date EH&S Officer
8/25/11 Violet Fanning Date Quality Assurance Manager	8/29/11 Tara Schlenker Date Laboratory Director

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1.0 Scope and Application

1.1 This method is for the preparation of sediments, sludges, and soil samples for analysis by ICPMS.

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become "environmentally available". By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment.

1.3 Please see Table 1 for elements that may be digested using this procedure.

- Additional elements may be prepared using this procedure, provided all appropriate QC measures are evaluated and found acceptable.
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1.5 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in the Quality Assurance Manual. **OVAP does not allow modifications to the SOP.**

2.0 Summary of Method

2.1 For the digestion of samples, a representative 1 gram sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). If lower reporting limits are required up to a 5 g sample may be used. Additional nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) may be required with the higher weight of sample.

2.2 The resultant digestate is reduced in volume while heating and then diluted to a final volume of 50 mL.

2.3 Hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed in order to stabilize silver and antimony.

2.4 If required, a separate sample aliquot must be dried for a total percent solids determination.

3.0 Definitions

3.1 Element- The Laboratory Information Management System.

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5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual (CW-E-M-001) 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

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

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 standards 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
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

- Hot Block / Hot Plate capable of maintaining temperatures of 95° C +/- 5 ^{o} C.
- Environmental Express Disposable screw cap Digestion Cups (SC475) – 50 mL (the manufacturer volume Certification for each lot is kept on file).
- Sample tubes, hinged caps, 70 mL or 100 ml NOTE: The 70 ml or 100 ml hinge cap tubes are not used for final volume determination.
- Macropipettes and micropipettes with disposable tips.
- Miscellaneous laboratory glassware and disposable plastic ware: All disposable plastic ware must be rinsed three times with deionized water before sample preparation. .
- Top loader balance capable of weighing to the nearest 0.01 gram. Analytical balance capable of weighing to the nearest 0.1 mg may be used when measuring very limited volume samples (such as paint chips and paint scrapings).
- Centrifuge and centrifuge tubes.
- Thermometer that has been calibrated against a NIST thermometer.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents 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 questionable, analyze the reagent to determine the level of impurities.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

All standards/reagents are stored at room temperature.

7.1 **Reagent Water**. Reagent water is interference free. All references to water in this SOP refer to reagent water unless otherwise specified. The Metals Department uses Deionized Water as Reagent Water.

7.2 **Nitric Acid (HNO_3), Concentrated:** Trace Metal grade or better. Shelf life is one year after opening or manufacturer's expiration date (whichever is shorter).

7.3 **Hydrochloric Acid (HCl), Concentrated:** Trace Metal grade or better. Self life is one year after opening or manufacturer's expiration date (whichever is shorter).

7.4 **Hydrogen peroxide (30%):** H_2O_2. Shelf life is one year after opening or manufacture's expiration (which ever is shorter)

7.5 **Quality Control Standard 21 from Spex**: (100 mg/L of As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn). Shelf life is one year after opening or manufacturer's expiration (which ever is shorter)

7.6 **Quality Control Standard 7 from Spex**: (1,000 mg/L of K; 100 mg/L of Ag, Al, B, Ba, Na; 50 mg/L of Si). Shelf life is one year after opening or manufacture's expiration (which ever is shorter)

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

8.2 OVAP and most other environmental samples require compliance with the information detailed in the analytical methods.

8.3

Matrix	Sample Container *	Min. Sample Size	Preservation	Holding Time	Reference
Soil	Plastic or glass	200 g	Chill to <6.0°C but not frozen.	180 days from sampling to analysis	40 CFR Part 136

*For concrete and other unusual matrices, the samples may be collected in plastic bottles, plastic bags or other containers.

8.4 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus, which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorbtion and (b) by depleting concentrations through adsorption, thus the collection and treatment of the sample prior to analysis requires particular attention. The quality control program must document through the use of spikes sample, reagent and sample blanks, that cleaning procedures are adequate. Care must be taken to verify the fact that the containers in which acid digested samples, blanks, and standards are packaged do not contribute contaminants.

9.0 Quality Control

9.1 The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency
Method Blank (MB)	1 per preparation batch[1]
Laboratory Control Sample (LCS)	1 per preparation batch[1]
Matrix Spike/Matrix Spike Duplicate (MS/MSD)[2]	1 per preparation batch[1]
Duplicate (DUP)[2]- Post Digestion Dilution Test	1 per preparation batch[1]
Post Spike [2]	1 per preparation batch[1]

[1]Preparation batch is limited to 20 samples
[2]The sample selection for MS/MSD/DUP and Post Spike is random, unless specifically requested by a client.

9.2 **Batching samples using ELEMENT**

9.2.1 One / Method Blank (MB). This is automatically added by ELEMENT. This MB is an aliquot of Deionized water that is carried through the digestion procedure and contains the same volumes of reagents as the sample solutions. Clean PTFE boiling chips are added to approximate the amount or weight of a sample to represent a non aqueous substance in the blank. The MB is useful in determining if samples are being contaminated from the reagents or environment.

9.2.2 One Laboratory Control Sample (LCS) This is automatically added by ELEMENT. The LCS/ is an aliquot of Deionized water that is spiked with a known concentration of metals and is carried through the same procedure as a sample would go through. , (same volumes of reagents). Clean PTFE boiling chips are added to approximate the amount or weight of a sample to represent a non aqueous substance in the LCS. The LCS is useful in determining accuracy by showing that a know concentration of metals can be taken through the procedure and recovered within the established acceptance limits.

9.2.3 One Matrix Spike (MS) / Matrix Spike Duplicate (MSD) pair. This is automatically added by ELEMENT; however, the digestion technician must select which sample to use for this pre-digestion spike requirement. This selected sample is digested three times: once non-spiked, once spiked as the MS, and once spiked as the MSD. The MS/MSD is spiked with a known concentration of metals. The MS/MSD is useful in determining precision and bias.

9.2.4 One Duplicate (DUP) to be designated as a Post-Digestion Dilution (1+4) Test Sample. This is automatically added by ELEMENT; however the preparations analysis must remove the DUP from the batch before saving. The instrumentation analyst must add the Duplicate back to the batch and select which sample to use for this post-digestion procedure and add a data qualification flag to indicate that it is a Post-Digestion Dilution (1+4) Test Sample rather than a duplicate digested sample.

9.2.5 One Post Spike (PS) to be designated as a Post-Digestion Spike sample. This is automatically added by ELEMENT; however the preparations analyst must remove the PS from the batch before saving. The instrumentation analyst must add the PS back to the back to the batch and selects which sample to use for this post-digestion procedure as well as document the appropriate spike solutions and amounts to be added.

9.3 Please see the analytical procedure SOP for acceptance criteria and corrective actions.

10.0 Procedure

10.1 All labware should be rinsed three times with deionized water before use during sample digestion. (70 ml plastic flip tops (SC601) and the 50 ml green screw digestion cups (SC475)

10.2 Mix the sample thoroughly to achieve homogeneity. If appropriate and necessary, a USS #10 sieve may be used. All equipment used for homogenization must be cleaned prior to use to minimize the potential of cross-contamination.

NOTE: All steps requiring the use of acids must be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment.

10.3 Into a 70 mL disposable plastic digestion vessel with a flip top lid, transfer a 1.0 – 1.09 g sample weighed to the nearest 0.01 g. For samples with high liquid content or that need a lower reporting limit, a larger sample size (usually 5.0 g) may be used as long as digestion is completed. For samples with limited amount and/or weighs less than 0.5 g use an Analytical Balance to weigh the sample, record the weight to 0.001g .

10.4 For the Method Blank (MB) and the Laboratory Control Sample (LCS) use approximately 5 mL of DI water and enough cleaned PTFE boiling chips to approximate the weight of sample used.

10.5 Add 5 mL of Deionized Water to all samples and MS/MSD.

10.6 To the Laboratory Control Sample (LCS) and to the Matrix Spike (MS) Matrix Spike Duplicate (MSD) vessels, add 0.5 mL of Quality Control Standard 21 from Spex and 0.5 mL of Quality Control Standard 7 from Spex using a macropipetter.

10.7 Add 5 mL of Concentrated HNO_3 (use a macropipetter or bottle top dispenser), mix the slurry, and cover the vessel loosely with the flip top lid .

10.8 Heat the sample to 95 C +/- 5 C and reflux for 10 to 15 minutes without boiling.

10.9 While still in the hot block add 5 ml of concentrated HNO_3 (use a macropipetter or bottle top dispenser), cover the vessel loosely with the flip top lid and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of conc. HNO_3) repeatedly until no brown fumes are given off by the sample indicating the complete reaction with HNO_3.

10.10 Continue to cover the vessel loosely with the flip top lid and either allow the solution to evaporate to approximately 10 mL without boiling or heat at 95°C $\pm$ 5°C without boiling for one and a half to two hours. Maintain a covering of solution over the bottom of the vessel at all times.

10.11 While still in the hot block add 3 mL of 30% H_2O_2 Using a new large disposable pipette for each addition of H_2O_2 and for each sample. Cover the vessel loosely with the flip top lid. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides.

10.12 Continue to add 30% H_2O_2 dropwise using a new disposable pipette for each addition of H_2O_2 and for each sample, while 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.

10.13 Cover the vessel loosely with the flip top lid and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 10 mL or heat at 95°C $\pm$ 5°C without boiling for 30 -45 min. Maintain a covering of solution over the bottom of the vessel at all times. Remove from hot plate.

10.14 While still in the hot block add 5 mL of concentrated HCl, use a macropipetter or bottle top dispenser, to the sample digestate, cover the vessel loosely with the flip top lid, and reflux for 15 minutes. Remove from hot plate.

10.15 After cooling, transfer the contents of the 70 mL flip top digestion vessel into an Environmental Express Disposable screw cap Digestion cup part # SC475. Rinse the digestion vessel at least three times with a small amount of deionized water and put the rinse solution into the SC475 screw cap digestion cup with the sample digestate. Bring to final volume of 50 mL with deionized water and mix well. At the discretion and preference of the instrumentation analysts, particulates in the digestate can then be removed by filtration, by centrifugation, or by allowing the sample to settle. The sample is ready for analysis.

10.16 In ELEMENT, under LABORATORY and BATCH, be sure to properly document the source and the amount of all standards, acids and reagents used; the initial weights and final volumes of each sample; the temperature reading from the thermometer, the label of hot block used for digestion and the date & time the digestion procedure was performed.

11.0 Calculations / Data Reduction - None Applicable.

12.0 Method Performance

The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.1 **Demonstration of Capabilities** – Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.2 **Method Detection Limit Study** – A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

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 accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.1 The following waste streams are produced when this method is carried out:

- Acidic waste containing nitric & hydrochloric acids is neutralized and discharged into the sanitary sewer.
- Contaminated disposable materials utilized for the analysis is disposed of in the general trash.

15.0 References / Cross-References

15.1 SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", 3rd Edition, Methods referenced are 3050B and 6020A.

15.2 DT-QA-005 Procedure for Balance Calibration Check

15.3 DT-QA-006 Thermometer Calibration

15.4 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.

15.5 This is an OVAP approved SOP. All changes must be approved by OVAP prior to implementation.

16.0 Method Modifications:

Item	Method	Modification
2.3	SW-3050B	For ICPMS, hydrochloric acid (HCl) is also added to the intial digestate and the sample is refluxed in order to stabilize silver and antimony.
7.2	SW-3050B	Instead of adding 10 mL of 1:1 HNO_3, we add 5 mL of Deionized Water and 5 mL of concentrated HNO_3 for this step. Also the sample are not removed from the heat source and allow to cool before the next step.
2 .2 & 7.4	SW-3050B	Final sample volume is 50 mL
4.8 and 7.2	SW-3050B	Section 4.8 calls for a temperature of 90-95 C, where section 7.2 says 95 +/- 5 C, this SOP uses 95 +/- 5 C.

17.0 Attachments

Table 1 Elements that may be digested using this procedures
Table 2 ICPMS Non Aqueous Prep 3050 outline

18.0 Revision History

18.1 Revision Dates

- 9/01/11 Biennial review
- 3/31/2009 replaces 8/23/2007

Section	Change from	Change to	Reason
1.3	Added	Additional elements may be prepared using this procedure, provided all	Clarification, consistency with other SOPs

Section	Change from	Change to	Reason
		appropriate QC measures are evaluated and found acceptable.	
1.4	Added	For OVAP, only compounds listed in the method may be reported using this procedure.	OVAP clarification
1.4	Added	Current default reporting limits are in the Laboratory Information Management System (LIMS). Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory specific method detection limit (MDL) data, project specific Data Quality Objectives (DQOs) and regulatory requirements are all taken into account.	Consistency with other SOPs
3.2	Added	Please see the Glossary in the Quality Assurance Manual, DT-QAM-001, for additional definitions.	Consistency with other SOPs
6	90° to 95°C	95° C +/- 5 ^{o} C.	Clarification of requirement
6	Environmental Express Disposable Digestion Cups	Environmental Express Disposable screw cap Digestion Cups (SC475)	Added screw cap and part number (SC475)
6	No thermometer statement	Thermometer that has been calibrated against a NIST thermometer.	Corrected equipment listing
7.4, 7.5 and 7.6	No statement about reagent shelf life	Shelf life is one year after opening or manufacture's expiration (which ever is shorter)	Clarification of requirement
9.2.1	No statement about adding clean PTFE boiling chips	Clean PTFE boiling chips are added to equal the amount or weight of a sample to represent a non aqueous substance in the blank.	Internal audit, missing information
Entire SOP	Removed	BS, Blank Spike	Improve naming convention consistency
8.1	Added	OVAP and most other environmental samples require compliance with the information detailed in the analytical methods.	VAP regulatory clarification

Section	Change from	Change to	Reason
8.3	Added	*For concrete and other unusual matrices, the samples may be collected in plastic bottles, plastic bags or other containers.	VAP clarification
9.2.2	No statement about adding clean PTFE boiling chips	Clean PTFE boiling chips are added to approximate the amount or weight of a sample to represent a non aqueous substance in the LCS.	Internal audit, missing information
9.2.4	This is automatically added by ELEMENT; however the instrumentation analyst	the preparations analysis must remove the DUP from the batch before saving. The instrumentation analyst must add the Duplicate back to the batch and selects which sample to use for this post-digestion procedure and adds a data qualification flag to indicate that it is a Post-Digestion Dilution (1+4) Test Sample rather than a duplicate digested sample	An Element change requires the Dup sample be selected at the time of saving the batch. The preparations analyst does not do this the instrument analyst does.
9.2.5	… however the instrumentation analyst selects which sample to use for this post-digestion procedure as well as document the appropriate	… however the preparations analyst must remove the PS from the batch before saving. The instrumentation analyst must add the PS back to the back to the batch and selects which sample to use for this post-digestion procedure as well as document the appropriate	An Element change requires the PS sample be selected and the spike and volume of the spike added at the time of saving the batch. The preparations analyst does not do this the instrument analyst does
9.3	Added	Please see the analytical procedure SOP for acceptance criteria and corrective actions.	Clarification of procedure
10.1	No statement about rinsing labware	All labware should be rinsed three times with deionized water before use during sample digestion. (70 ml plastic flip tops (SC601) and the 50 ml green screw digestion cups (SC475)	Internal audit, missing information
10.3	No statement as to when it is necessary to use the analytical balance	For samples with limited amount and/or weighs less than 0.5 g the Analytical Balance in the instrumentation lab must be used to weigh the sample, record the weight to 0.001g.	Internal audit, missing information
Entire SOP	Removed	PB, Blk, Preparation Blank	Improve naming convention consistency
10.4	No statement about adding PTFE boiling chips	and enough cleaned PTFE boiling chips to equal the amount or weight of sample used.	Include a statement about adding PTFE boiling chips

Section	Change from	Change to	Reason
10.5	Not specified to add 5mlwater to MS/MSD	MS/MSD	To specify to add 5 ml water to the MS/MSD
10.7 & 10.9 & 10.14	Not specified how to add the reagent	(use a macropipetter or bottle top dispenser),	Add a statement indication how to add the reagent
10.9, 10.11 & 10.14	Remove from hot block and allow to cool	While still in the hot block	Clarification of instructions
10.11	Not specified how to add the H_2O_2	Using a new large disposable pipette for each addition of H_2O_2 and for each sample	Specify how to add the H_2O_2
10.12	Not specified how to add the H_2O_2	dropwise using a new disposable pipette for each addition of H_2O_2 and for each sample, while	Specify how to add the H_2O_2
10.15	Not enough detailed instructions to analytically transfer and bring the sample to volume	70 mL flip top digestion vessel into an Environmental Express Disposable screw cap Digestion cup part # SC475. Rinse the digestion vessel at least three times with a small amount of deionized water and put the rinse solution into the SC475 screw cap digestion cup with the sample digestate	Provide enough detailed instructions to analytically transfer and bring the sample to volume
Tables	Added	Table 2 ICPMS Non Aqueous Prep 3050 outline (may be posted in laboratory as a separate sheet)	

Table 1 Elements that may be digested using this procedure

Aluminum	Lead
Antimony	Manganese
Arsenic	Molybdenum
Barium	Nickel
Beryllium	Selenium
Cadmium	Silver
Chromium	Thallium
Cobalt	Vanadium
Copper	Zinc
Iron	Strontium
Titanium	

Table 2 ICPMS Non Aqueous Prep 3050 outline (may be posted in laboratory as a separate sheet)

This outline does not replace the SOP. Use of this outline is restricted to analysts who have read, and been approved to conduct procedures as described in, the affiliated SOP.

1. Rinse containers three times with deionized water
2. Weigh samples in flip top containers
   a. Samples are usually weighed out to 1.0g
   b. Some samples have specific RLs or have special comments to be weighed out to 5.0g. Paint chips are also special weights of 0.50g.
   c. If not sure, ask Dept Manager or the analyst
3. Add ~5mL DI water to each sample
4. In Blank and BS also add ~5 boiling chips
5. SPIKES:
   - 0.50mL of QC 7 in BS, MS, MSD (500uL)
   - 0.50mL of QC 21 in BS, MS, MSD (500uL)
6. Add 5mL of conc. Nitric acid to each sample
7. Place samples in Mod Block
8. Cook and reflux for 10 to 15 minutes, without boiling
9. Add 5 mL conc Nitric acid
10. Cover loosely and reflux for 30 minutes
11. If brown fumes are generated, repeat additions of 5mL conc Nitric and heat until fumes are no longer given off.
12. Cook down to a little over 10mL (1.5 to 2 hours)

NOTE: Make sure samples do not go below 5mL

13. Add ~3mL to Hydrogen Peroxide (large disposable pipette is about 3mL when full)

NOTE: Be careful when adding because samples will boil over and possibly contaminate the other samples. Add VERY slowly to every sample or add a couple drops to a couple of samples and switch back and forth.

14. Continue to add 30% Hydrogen Peroxide drop-wise while warming until effervescence is minimal or sample appears unchanged

NOTE: Do not add more than a total of 10mL peroxide

15. Cook samples back down to 10mL (30 – 45 minutes)
16. Add 5mL of concentrated Hydrochloric acid
17. Reflux 15 minutes
18. Take samples out of Mod Block
19. Let samples cool ~15minutes
20. Pour from large flip top into <u>labeled</u> green screw cap containers
    a. Make sure to rinse flip top container with DI water and pour water into the green screw cap container, making sure to get as much sample out of the flip top as possible.
21. Fill green screw cap containers up to 50mL with DI water
22. Take to ICPMS analyst

Title: SW 6010A/B- Inductively Coupled Plasma-Atomic Emission Spectrometry

USEPA SW-846 6010A/B

Approvals (Signature/Date):

9/10/07	9/10/07
Jason Lykins — Date	Jan Grover — Date
Department Manager / Supervisor	Health & Safety Manager / Coordinator
9/10/07	9/10/07
Violet Fanning — Date	Deborah Lowe — Date
Quality Assurance Manager	Laboratory Director

This SOP was previously referenced as DT04-26, rev 4.

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1.0 Scope & Application

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Tables 1a and 1b. All matrices, excluding filtered groundwater samples but including groundwater, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludge, sediments, and other solid wastes, require digestion prior to analysis. Ground water samples that have been pre-filtered and acidified do not require digestion. Samples that are not digested must either use an internal standard or be matrix matched with the standards. Please see the appropriate digestion SOPs for additional preparation information.

1.2 Detection limits, sensitivity, and the linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix, and operating conditions. Tables 1a and 1 b list the analytical wavelengths and background correction points. Table 2 lists the standard reporting limits for aqueous and non-aqueous samples and the linear range for each element.

1.3 Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method.

1.5 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis with the supporting demonstration of sensitivity and accuracy (e.g. MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into project special instructions (e.g. Quality Assurance Project Plans), authorized by the laboratory, and mentioned in the report narrative. **OVAP does not allow changes to the SOP.**

2.0 Summary of Method

2.1 Prior to analysis, samples must be solubilized or digested using appropriate ICP Sample Preparation SOPs. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multi-elemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a

background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 4 should also be recognized and appropriate corrections made; tests for their presence are described in Section 9.

3.0 Definitions

3.1 ELEMENT- The Laboratory Information Management System

3.2 Dissolved Metals – those constituents (metals) that will pass through a 0.45 um membrane filter.

3.3 Suspended Metals – those constituents (metals) that are retained by a 0.45 um membrane filter.

3.4 Total Metals – the concentration of metals on an unfiltered sample following vigorous digestion or the sum of the dissolved and suspended metals.

3.5 SIC – Spectral Interference Check – used to establish that the ICP is free from spectral interferences

4.0 Interferences

4.1 Spectral interferences are caused by background emission from continuous 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.

4.1.1 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 spectral interferences are handled by including spectra on interfering species in the algorithm.

4.1.2 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 interference effects from all method analytes and common elements and

provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. 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.

4.1.3 Spectral overlaps may be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements are 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 interferent 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.

4.1.4 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 interfering 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.

4.1.5 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 argon flow rate). When using the recommended wavelengths, the analyst 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 or matrix. The analyst must utilize a computer routine for automatic correction on all analyses.

4.1.6 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. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

4.1.7 When inter-element 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

the 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 be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

4.2 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. The Dilution Test described in Section 9 will help determine if a physical interference is present.

4.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4 Memory interferences result when analyses 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 element 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. 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 Data Quality Objectives

4.5 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.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and 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

The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

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 standards 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
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, and productivity. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Inductively coupled argon plasma emission spectrometer:

- 6.1.1 Computer-controlled emission spectrometer with background correction.
- 6.1.2 Radio-frequency generator compliant with FCC regulations.
- 6.1.3 Peristaltic pump.
- 6.1.4 Autosampler.

6.2 Argon gas supply - high purity.

6.3 Miscellaneous Laboratory Glassware and plasticware

6.4 Miscellaneous Macro and Micro Pipettes

6.5 Analytical Balance capable of weighing to the nearest 0.1 mg.

6.6 Autosampler tubes with and without caps.

6.7 Environmental Express Disposable Digestion Cups – 50 mL with caps (the manufacturer Volume Certification for each lot is kept on file).

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, or productivity. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

All standards/Reagents may be stored at room temperature.

7.1 Reagent or trace metals grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must 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 of the contamination is less than the MDL then the reagent is acceptable.

7.2 Hydrochloric acid (conc.), HCl. Shelf life: one year after opening or manufacturer expiration date (which ever is shorter).

7.3 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in a Volumetric Flask. Shelf life: one year after preparation or manufacturer expiration date (which ever is shorter).

7.4 Nitric acid (conc.), HNO_3. Shelf life: one year after opening or manufacturer expiration date (which ever is shorter).

7.5 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO3 to 400 mL water and dilute to 1 liter in a Volumetric Flask. Shelf life: one year after preparation or manufacturer expiration date (which ever is shorter).

7.6 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. The Metals Department uses Deionized Water as reagent water.

7.7 Standard stock solutions are purchased. Refer to Tables 4a & 4b for the shelf life of the standards.

7.8 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Tables 4a & 4b). Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Refer to Tables 4a & 4b for the shelf life of the mixed calibration standard solutions.

7.8.1 NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.9 Two types of blanks are required for the analysis of digested samples. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing.

7.9.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. The calibration blank will also be used for all initial and continuing calibration blank determinations.

7.9.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.10 The Initial Calibration Verification (ICV)is prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard and at concentrations within the linear working range of the instrument (See Tables 4a & 4b for preparation).

7.11 The Continuing Calibration Verification (CCV) should be prepared in the same acid matrix as the calibration standards (See Tables 4a & 4b for preparation).

7.12 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 and 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. However, due to the fact that the ICP instruments used in this laboratory will display overcorrection as a negative number, this spiking procedure will not be necessary (See Tables 4a & 4b for preparation).

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Aqueous samples:

8.1.1 Samples should be collected in plastic or glass containers with a minimum size of 250 mL.

8.1.2 Samples are preserved with 25 % HNO3 (8 mL of acid per Liter) at the time of collection. Proper preservation (pH <2) is checked prior to digestion. This is documented in the ICP Preparation Log.

8.1.3 If samples are found to be pH >2, then additional HNO3 is added. The sample must be held for at least 24 hours after preservation, except drinking waters which must be held for at least 16 hours.

8.1.4 Samples have a hold time of 180 days prior to analysis if preserved at a pH of <2.

8.1.5 Samples are not required to be refrigerated

8.2 Non-Aqueous Samples:

8.2.1 Samples should be collected in plastic or glass containers with a minimum size of 200 g.

8.2.2 Samples have a hold time of 180 days prior to analysis.

8.2.3 Samples are required to be refrigerated.

9.0 Quality Control

9.1 All quality control data must be maintained and available for easy reference or inspection.

9.2 Initial Calibration Verification Standard (ICV) / Continuing Calibration Verification Standard (CCV)

9.2.1 Analyze the ICV immediately following a calibration curve to verify the curve. The percent recovery acceptance criteria is +/- 10% of the true value.

- If the ICV fails, it may be repeated one time. If the repeated ICV passes, you may proceed with the analytical sequence.
- If the repeated ICV fails, the analytical sequence must be terminated and the problem investigated. First, verify that the ICV standard was prepared correctly. If the preparation is questionable, re-prepare the ICV standard and reanalyze. If the re-prepared ICV standard passes and it is determined that the first ICV standard was incorrectly prepared, the analytical sequence may proceed.

NOTE: No sample can be run prior to a passing ICV.

- If the re-prepared ICV standard also fails, further investigation is required. Verify that the calibration blank and standards were prepared correctly. Check the instrument nebulizer, spraychamber, torch, and autosampler tubing for clogged or poor connections. If any of these items are determined to be the cause of the problem, the items must be fixed. Since you may not be able to determine if this problem occurred before, during, or after the calibration, the entire analytical sequence, including instrument profile checks, calibration, and instrument QC check standards must be repeated.

9.2.2 Analyze the CCV after all of the other initial instrument QC samples (ICB, ICV, RLVs, and SICs) have been analyzed, but before analyzing sample batches, after every 10th sample and at the end of the analytical sequence. The percent recovery acceptance criteria is ± 10% of the true value.

- If the CCV fails, it may be repeated one time. If the repeated CCV passes, you may proceed with the analytical sequence. If the repeated CCV fails, the analytical sequence must be terminated and the problem investigated.
- If the failure is with the first CCV in the sequence, verify that the CCV standard was prepared correctly. If the preparation is questionable, re-prepare the CCV standard and reanalyze. A retained portion of the original CCV preparation may be useful in troubleshooting. If the re-prepared CCV standard passes and it is determined that the first CCV standard was incorrectly prepared, the analytical sequence may proceed.
- If the re-prepared CCV standard also fails, further investigation is required. Check the instrument nebulizer, spraychamber, torch, and autosampler tubing for clogged or poor connections. If any of these items are determined to be the cause of the problem, the items must be fixed. In an effort to save time, after fixing the problem, you may reanalyze the instrument QC check standards (ICB, ICV, RLVs, and SICs) and continue with the analytical sequence without repeating the entire instrument profile and calibration. This is acceptable if you are able to determine that the problem occurred after the calibration curve was verified by the passing ICV Standard (a secondary source). Note that no sample batches have been analyzed yet.

9.2.3 During the course of an analytical sequence, the instrument may drift as a result of varying temperature and humidity changes in the room. If drift is suspected, the instrument may be re - profiled.

9.2.4 If the CCV that fails is not the first CCV in the sequence, incorrect preparation of the CCV would not be suspected. Investigate the system as in 9.2.2. Determine if re-profiling is necessary. If any of these issues are determined to be a problem they must be fixed.

- After fixing the problem and analyzing a passing CCV, to ensure that the problem has been fixed, sample analysis may continue. Recalibration is not necessary because it has been determined that the isolated problem occurred between a passing CCV and a failing CCV. Any samples analyzed since the last acceptable CCV must be re-analyzed.

9.3 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

9.3.1 Analyze the ICB immediately following a calibration curve to verify the curve. Analyze the CCB after every 10th sample and at the end of the analytical sequence. The following limits are monitored:

- If a value is greater than the Method Reporting Limit (MRL), all samples between that CCB and the previous passing CCB must be re-analyzed for that failing parameter.
- When analyzing samples that get reported down to the MDL, if a value is greater than the MDL but less than the MRL, all samples with hits above the MDL will be reported as-is with an appropriate data qualification flag.
- For all OVAP samples, contamination must be less than the Method Reporting Limit (MRL).

9.4 Method Blank (MB or BLK)

9.4.1 Analyze a minimum of one method blank (BLK) with each prep batch of 20 or fewer samples. This method blank is carried through the same procedures as a sample would go through. The following limits are monitored:

9.4.2 If a value is greater than the Method Reporting Limit (MRL), all samples in that batch must be re-digested and re-analyzed for that failing parameter. The exception is when the concentration in the blank of any analyte of concern is less than 5% of the measured concentration of the sample; the blank contamination is determined to be insignificant and the data is flagged. If a sample cannot be re-digested and re-analyzed, the data will be reported with an appropriate data qualification flag.

- When analyzing samples that get reported down to the MDL, if a value is greater than the MDL but less than the MRL, all samples with hits above the MDL will be reported as-is with an appropriate data qualification flag.
- For all OVAP samples, contamination must be less than the Method Reporting Limit (MRL).

9.5 Laboratory Control Standard (LCS) / Blank Spike (BS)

9.5.1 Analyze one laboratory control standard (LCS) per every batch of 20 or fewer samples. The LCS is carried through the same procedure as a sample would go through. The current acceptance limits are located in the QA Manual. If the LCS is outside the acceptance limits for a particular parameter, it may be repeated one time. If the LCS is still outside of the acceptance limits, all samples prepared

with the LCS in the batch must be re-prepped/reanalyzed for that parameter with the following exception:

9.5.2 High Bias LCS recovery. In the event that a LCS recovery fails high for a specific parameter, associated samples in that batch are not required to be re-digested and re-analyzed if there was no detection for that parameter in those samples.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1 The MS/MSD pair are two sample aliquots spiked at known concentration that must be analyzed per every batch of 20 or fewer samples. These spikes must be carried through the same procedures, as a sample would go through. The current acceptance limits are located in the QA Manual. If the MS/MSD recoveries are not within the required acceptance limits, the MS/MSD results are reported with an appropriate data qualification flag.

9.6.2 The MS/MSD are not used for batch control.

9.7 Reporting Limit Verification Standards (RLVs)

9.7.1 The RLVs are standards that have concentrations at or below the established method reporting limits (MRLs) that are run after the instrument calibration. The acceptance criterion for this standard is ± 30% of the true value. If this criterion does not pass, the samples in the run must be repeated unless the following provisions are followed:

9.7.2 If the RLV recovery is high, and the samples are non-detect for that specific analyte, then the data may be reported with flags.

9.7.3 If the samples being analyzed have client required MRLs or permit limits that are greater than our standard MRLs, then the MRL may be elevated to the higher value of another passing RLV standard, or to the level of the lowest point in the calibration curve.

9.8 Internal Standards (IS)

9.8.1 The Internal Standards are elements that are similar to the elements that are being analyzed. Both ICP instruments used in this laboratory use Yttrium as the Internal Standard to be added to all samples and QC samples. The TJA 61E Trace ICP automatically adds a consistent amount of internal standard to every sample prior to being nebulized into the spray chamber. Samples analyzed on the Perkin Elmer 4300DV ICP must have internal standard manually added to an aliquot of sample prior to analysis (100uL of 60 mg/L Yttrium per 10 mL of sample). The absolute response of any one internal standard must not deviate more than 70-130 % of the original response in the calibration blank.

9.8.2 The intensities of the internal standard must be monitored for every analysis. If the intensity of the internal standard in a sample deviates more than 70-130% of the intensity of that internal standard in the initial calibration blank, a significant matrix effect must be suspected. Under these conditions, the detection limit has degraded and the correction ability of the internal standardization technique becomes questionable. The following procedure is followed: First, make sure the instrument has not just drifted by observing the internal standard intensities in

the nearest clean matrix (initial calibration blank (ICB) or continuing calibration blank (CCB)). If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples. Unless there is an obvious matrix interference, which may be suggested if several samples following the first failing sample also have failing internal standards due to some complex carry-over problem, you should try to reanalyze the sample without dilution to verify that a matrix interference problem exists. After you have verified that a matrix interference exits, and have determined that instrument drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted twofold (1+1) or fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities fall within the 70-130 percent limit. Reported results must be corrected for all dilutions and with an appropriate data qualification flag.

9.8.3 While the criteria for Internal Standard recoveries for quality control standards (ICB, ICV, ICSA, ICSAB, RLVs, CCB, CCV, BLK, and BS) is not stated in Method 6010B, this laboratory has established that the internal standard must not deviate more than 70-130% of the original response in the calibration blank. If these requirements are not met, the solutions must be re-analyzed (or fresh solutions re-made and then re-analyzed). If these requirements are still not met, the analysis must be terminated, the problem corrected (to include such items as general instrument maintenance, cleaning, and conditioning), the instrument recalibrated and any affected samples reanalyzed.

9.9 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined below, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

9.9.1 Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:5 dilution must agree within +/- 10% of the original determination. If not, a chemical or physical interference effect should be suspected

9.9.2 Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, must be recovered to within 75% to 125% of the known value. The spike addition must 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.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with another method is recommended.

9.10 <u>Linear Range Analysis (LRA)</u>

9.10.1 The LRA is run annually or whenever is major change for instrumentation/standardization takes place. The linear range is established by analyzing multiple standards to determine the maximum concentration that each analyte is linear. The LRA recoveries must be within +/- 10% of the true value.

9.10.2 Samples with results greater than 90% of the LRA must be diluted and re-analyzed. The analyst must also be aware that if an interelement correction from

an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported.

9.10.3 Table 2 lists the current Linear Range Limits, which are subject to change based on the LRA study.

9.11 Interelement Correction (IECs) factors for all elements must be verified for all elements every 6 months. This is accomplished by analyzing single element standard solutions of each element at the upper linear range. The IECs are adjusted until all non-spiked metals are within ± reporting limit of zero.

9.12 Verify the interelement and background correction factors at the beginning of each analytical run. Do this by analyzing Spectral Interference Check (SIC) samples. Please see Tables 4a & 4b for Preparation and Concentration Information. Results of the metals not present in the SIC solutions must be less than ± the reporting limit to demonstrate that the Interelement Corrections are working properly. The results of the metals not present in the SICs that are greater than ± ½ the reporting limit, but less than ± the reporting limit must be monitored closely. The IEC are calculated by dividing the apparent metal concentration by the interferent concentration.

9.13 TCLP Quality Assurance Indicators (Only for TCLP):

9.13.1 For TCLP extract analyses, all calibration, sample handling and quality control procedures in this SOP must be followed with the addition of the following TCLP procedures.

9.13.2 Extraction Blanks: A TCLP extraction blank must be analyzed periodically to ensure that the process is free of analyte contamination. One extraction blank must be analyzed for every 20 extractions performed per type of extraction fluid. The extraction blank must be less than the analytical reporting limit for each analyte of interest. For analyte detections in the blank which are above the reporting limit, the extraction and preparation process must be suspended and investigated to determine the cause of the contamination and take corrective action. Any affected samples must be re-extracted, re-digested, and reanalyzed.

9.13.3 Matrix Spikes: A matrix spike must be performed periodically to assess analyte recovery in the matrix type. Matrix spikes are to be added after extract filtration. Matrix spikes are not to be added prior to the extraction process. See Tables 4a & 4b for spiking procedure and concentration. Matrix spikes are performed at a frequency of one per 20 samples. The current acceptance limits are located in the QA Manual. However, if the recovery is not greater than 50% of the spiked value, if the concentration of the analyte is more than 4 times that of the spike, or if the matrix spike sample must be diluted to be brought into calibration range, then the Method of Standard Additions (MSA) can be used to assess analyte concentration. All samples that are spiked properly and still have unacceptable recoveries can be analyzed using the MSA.

9.13.4 Method of Standard Additions (MSA): MSA requires 4 identical aliquots of the sample, 3 of which are spiked with known amounts of standard. The fourth aliquot is the unknown. The first standard addition must be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third standard additions must be prepared so that the concentrations are 100% and 150% of the expected sample concentration. All 4 aliquots are maintained at the same final volume by adding reagent water or blank solution and may need dilution adjustment to maintain the signals in the

linear range of the instrument technique. All four aliquots are then analyzed. A linear regression plot of instrument signals as the dependent variable (y-axis) vs. standard concentration of the additions as the independent variable (x-axis). Solve the plot for the abscissa (x-axis intercept), which will be the concentration of the unknown (prior to taking into account any dilution factors).

10.0 Procedure

10.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples that are not digested must either use an internal standard or be matrix matched with the standards. Solubilization and digestion procedures are presented in Sample Preparation SOPs.

10.2 Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration). Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer.

10.2.1 Before using this procedure to analyze samples, there must be data available documenting initial demonstration of performance. The required data document the selection criteria of background correction points; analytical dynamic ranges, the applicable equations, and the upper limits of those ranges; the method and instrument detection limits; and the determination and verification of interelement correction equations or other routines for correcting spectral interferences. This data must be generated using the same instrument, operating conditions and calibration routine to be used for sample analysis. These documented data must be kept on file and be available for review by the data user or auditor.

10.2.2 Specific wavelengths and background correction points are listed in Tables 1a & 1b. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a task.

10.2.3 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array.

- Ignite the plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. While aspirating a solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the load coil. The yttrium solution can also be used for coarse optical alignment of the torch by observing the overlay of the blue light over the entrance slit to the optical system.
- After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume of

calibration blank for a period of at least three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate; set the peristaltic pump to deliver the rate in a steady even flow. Record in the maintenance log

- Profile the instrument to align it optically with the Arsenic Profiling Solution. Please see Tables 4a & 4b for Preparation and Concentration Information. The peak position must be within ± 0.10 units. Adjust alignment if not within limits. Record peak intensity and peak position.
- The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits.
- If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and viewing height should be re-optimized.

10.2.4 Before daily calibration and after the instrument warm-up period, the nebulizer gas flow rate must be reset to the determined optimized flow.

10.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Tables 4a & 4b. Flush the system with the rinse solution that approximately matches the standards/samples between each standard. The calibration curve must consist of a minimum of a blank and a standard. Use the average intensity of three exposures for both standardization and sample analysis to reduce random error. If the Relative Standard Deviation (RSD) of the three replicates exceed 10% on readings that are above the Method Reporting Limit (MRL) for any target element, that sample or standard must be reanalyzed. If the RSD of the reanalysis of a sample also exceeds 10%, a sample matrix interference may be suspected and further evaluation (i.e. dilution test and/or post-digestion spike) and proper data qualification flags are required. If more than one sample and/or “interference-free” QC samples are having RSDs exceeding 10%, check the instrument nebulizer, spraychamber, torch, and autosampler tubing for clogged or poor connections.

10.4 For all analyses and determinations, the laboratory must analyze an ICV and a continuing calibration blank immediately following daily calibration. A calibration blank and either a calibration verification (CCV) or an ICV must be analyzed after every tenth sample and at the end of the sample run. Analysis of the check standard and calibration verification must verify that the instrument is within +/- 10% of the true value. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV, CCV or check standard must be reanalyzed. The analysis data of the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

10.5 Rinse the system before the analysis of each sample. The rinse time will be a minimum of one minute unless the laboratory can demonstrate a shorter rinse time is acceptable.

10.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values.

10.7 MSA is performed only upon client request. The MSA should be used if an interference is suspected or a new matrix is encountered. When the method of standard additions is

used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement of depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by: multiplying the intensity value for t he unfortified aliquot by the volume (Liters) and the concentration (mg/L or mg/Kg) of the standard addition to make the numerator; the difference in intensities for the fortified sample and unfortified sample is multiplied by the volme (Liters) of the sample aliquot for the denominator. The quotient is the sample concentration. For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution. Refer to Method 7000 for a more detailed discussion of the MSA.

10.8 An alternative to using the method of standard additions is the internal standard technique. Add one or more elements not in the samples and verified not to cause an interelement spectral interference to the samples, standards and blanks; yttrium or scandium are often used. The concentration should be sufficient for optimum precision but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences especially in high solids matrices.

NOTE: This laboratory utilizes the internal standard technique, instead of MSA, on both of the ICP instruments used for metals analysis.

11.0 **Calculations / Data Reduction**

11.1 All calculations for all analyses (standards and samples) are based on the average of three replicate instrument readings.

11.2 Aqueous Sample Concentration

$$SC = \frac{IR \times V_f}{V_i}$$

Where:

SC = Aqueous Sample Concentration in mg/L

IR = Instrument response in mg/L

V_f = Final Volume in mL

Vi = Initial Volume in mL

11.3 Non-Aqueous Sample Concentration

$$SC = \frac{IR \times V_f}{W_i}$$

Where:

SC = Non-Aqueous Sample Concentration in mg/Kg

IR = Instrument response in mg/L

V_f = Final Volume in mL

Wi = Initial Weight in grams

11.4 Relative Percent Difference (RPD) between Duplicates:

$$RPD = \frac{(\text{Larger Value} - \text{Smaller Value}) \times 100}{(\text{Average of the Values})}$$

11.5 Spike Recovery of Laboratory Control Standards, Matrix Spikes, and Matrix Spike Duplicates:

$$\%\text{Recovery} = \frac{C - C_x}{(C_{SP})} \times 100$$

Where:

C = Concentration of Metal in Matrix Spike, Matrix Spike Duplicate, or LCS

C_X = Concentration of Metal in unspiked sample (above RL, assume 0 for concentrations <RL). C_x = 0 in the LCS.

C_{sp} = Spike level.

11.6 Silica, mg/L = (2.14) X (Silicon conc. mg/L)

11.7 Potash (K_2O), mg/L = (1.205) X (Potassium conc. mg/L)

11.8 Hardness (calculated), mg/L = ((2.497) X (Ca. mg/L)) + ((4.118) X (Mg, mg/L))

11.9 Trivalent Chromium (calculated), mg/L = (Cr, mg/L) – (Cr^{+6}, mg/L)

12.0 Method Performance

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study - A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.4 Instrument Detection Limits Study - An IDL must be determined at least every three months and kept with the instrument logbook.

13.0 Waste Management and 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).

13.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in the Environmental Health & Safety Manual for "Waste Management and Pollution Prevention."

13.2 The following waste streams are produced when this method is carried out:

13.2.1 Acid waste consisting of sample and rinse solution is neutralized and discharged to the sanitary sewer.

14.0 References / Cross-References

14.1 SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", 3rd Edition, Methods referenced are 6010A and 6010B ICP

15.0 Method Modifications

Item	Method	Modification
3.1.10	SW-6010B	Section Not Applicable. Inter-element Correction Factors are used.

16.0 Attachments

Table 1a TJA 61E Trace Operating Conditions
Table 1b PE Optima 4300 DV ICP
Table 2 Example Reporting Limits and Linear Ranges
Table 3 Premixed Solutions
Table 4a Preparation of Solutions (TJA 61E Trace ICP)
Table 4b Preparation of Solutions ((PE Optima 4300 DV ICP)
Table 5a Final Concentrations ((PE Optima 4300 DV ICP)
Table 5b Final Concentrations(TJA 61E Trace ICP)

17.0 Revision History

Revision dated 9/14/07

- Review for OVAP Compliance Audit

18.0 Contingencies

If for any reason a part of this SOP cannot be followed, seek the guidance of the Department Supervisor or Quality Assurance Department. Document all deviations on a Corrective Action Report and submit to the QA Quality Assurance Department.

This is an OVAP approved SOP. All changes, other than formatting or spelling, made to this SOP must be approved by OVAP prior to implementation.

Table 1a: TJA 61E Trace ICP Operating Conditions:

Element	Wavelength	Background Correction Point Location
Aluminum	308.215	17
Antimony	206.838	17
Arsenic	189.042	-19
Barium	493.409	-19
Beryllium	313.042	-19
Boron	249.670	17
Calcium	317.933	-19
Cadmium	226.502	17
Chromium	267.716	-19
Cobalt	228.616	17
Copper	324.753	17
Iron	271.441	17
Iron	259.94	-19
Lead	220.351	-19
Lead	220.352/2	17
Magnesium	279.079	17
Manganese	257.610	17
Molybdenum	202.030	17
Nickel	231.604	-19
Potassium	766.491	N/A
Selenium	196.021	-19
Selenium	196.022/2	17
Silicon	251.612	-19
Silver	328.068	-19
Sodium	589.995	N/A
Thallium	190.864	-19
Tin	189.989	-19
Titanium	334.941	17
Vanadium	292.402	-19
Yttriun	360.063	-19
Zinc	206.200	17

Table 1b: PE Optima 4300 DV ICP Operating Conditions.				
Element	Wavelength	View	No. of Points	Background Correction Point Location
Aluminum	308.215	Radial	1	-0.028
Antimony	206.836	Axial	2	-0.025; 0.037
Arsenic	188.979	Axial	1	0.034
Barium	233.527	Radial	1	0.055
Beryllium	313.042	Radial	2	-0.061; 0.110
Boron	249.677	Axial	1	0.040
Calcium	315.887	Radial	2	-0.057; 0.064
Cadmium	228.502	Axial	1	0.045
Chromium	267.708	Axial	1	-0.098
Cobalt	228.615	Axial	2	-0.035; 0.039
Copper	327.393	Axial	1	-0.055
Iron	238.204	Radial	1	0.050
Lithium	670.784	Radial	2	-0.121; 0.103
Lead	220.354	Axial	2	-0.034; 0.038
Magnesium	279.077	Radial	2	-0.050; 0.058
Manganese	257.610	Radial	1	0.134
Molybdenum	202.032	Axial	1	-0.031
Nickel	231.607	Axial	1	-0.043
Potassium	766.490	Radial	2	-0.134; 0.121
Selenium	196.026	Axial	1	0.024
Silicon	-	-	-	-
Silver	328.068	Axial	1	-0.029
Sodium	589.592	Radial	2	-0.144; 0.082
Strontium	460.733	Radial	2	-0.060; 0.071
Thallium	190.802	Axial	1	0.046
Tin	189.927	Axial	1	0.064
Titanium	334.940	Radial	1	0.163
Vanadium	292.402	Radial	1	-0.030
Zinc	206.200	Axial	1	-0.083

Table 2: Example Reporting limits and Linear Ranges

Element	Standard Aqueous Reporting Limit (mg/L)	Standard Non-Aqueous Reporting Limit (mg/Kg) *	PE Optima 4300 DV ICP Linear Range (mg/L)	TJA 61E Trace ICP Linear Range (mg/L)
Aluminum	0.100	16.7	2000	500
Antimony	0.100	16.7	25	25
Arsenic	0.100	16.7	25	25
Barium	0.020	3.33	200	25
Beryllium	0.0050	0.833	25	10
Boron	0.050	8.33	50	50
Calcium	1.0	167	2000	500
Cadmium	0.030	5.00	25	10
Chromium	0.040	6.67	25	25
Cobalt	0.020	3.33	100	25
Copper	0.020	3.33	100	50
Iron	0.100	16.7	500	500
Lead	0.080	13.3	500	25
Lithium	0.010	1.67	100	N/A
Magnesium	1.0	167	2000	500
Manganese	0.010	1.67	100	10
Molybdenum	0.020	3.33	25	50
Nickel	0.010	1.67	100	50
Potassium	1.0	167	1000	N/A
Selenium	0.100	16.7	25	25
Silicon	0.5	83.3	N/A	25
Silver	0.040	6.67	5	2
Sodium	1.0	167	1000	N/A
Strontium	0.10	16.7	50	N/A
Thallium	0.10	16.7	100	50
Tin	0.05	8.33	50	50
Titanium	0.020	3.33	50	10
Vanadium	0.050	8.33	100	25
Zinc	0.050	8.33	25	25

* Based on 1.5 grams of sample prepped to a final volume of 50 mL and a post-digestion 5X dilution.

Table 3: Premixed Solutions used

- MIXSTD 1; Spex Catalog # MIXSTD1-100 or EM Science Catalog #EP60101-1

Be	50 mg/L	Mn	100 mg/L
Cd	150 mg/L	Se	200 mg/L
Pb	500 mg/L	Zn	150 mg/L

- MIXSTD 2: Spex Catalog # MIXSTD2-100

Fe	1000 mg/L	Cu	100 mg/L
Ba	100 mg/L	V	100 mg/L
Co	100 mg/L		

- MIXSTD 5: Spex Catalog # MIXSTD5-100 or EM Science Catalog #EP60105-1

Sb	200 mg/L	Ag	50 mg/L
B	100 mg/L	Tl	200 mg/L
Mg	1000 mg/L		

- QC 7: Spex Catalog # QC 7-500 or Ultra Scientific Catalog #IQC-007

Al	100 mg/L	Si	50 mg/L
Ba	100 mg/L	Ag	100 mg/L
B	100 mg/L	Na	100 mg/L
K	1000 mg/L		

- QC 7: Environmental Express# ICQ 500-7

Al	100 mg/L	Si	50 mg/L
Ba	100 mg/L	Ag	100 mg/L
B	100 mg/L	Na	100 mg/L
K	1000 mg/L		

- QC 21: Spex Catalog # QC 21-500

Sb	100 mg/L	Sr	100 mg/L
As	100 mg/L	Mg	100 mg/L
Be	100 mg/L	Mn	100 mg/L
Cd	100 mg/L	Mo	100 mg/L
Ca	100 mg/L	Ni	100 mg/L
Cr	100 mg/L	Se	100 mg/L
Co	100 mg/L	Tl	100 mg/L
Cu	100 mg/L	Ti	100 mg/L
Fe	100 mg/L	V	100 mg/L
Pb	100 mg/L	Zn	100 mg/L
Li	100 mg/L		

Table 3: Premixed Solutions used (continued)

- QC 21: Environmental Express ICQ 500-21

Sb	100 mg/L	Sr	100 mg/L
As	100 mg/L	Mg	100 mg/L
Be	100 mg/L	Mn	100 mg/L
Cd	100 mg/L	Mo	100 mg/L
Ca	100 mg/L	Ni	100 mg/L
Cr	100 mg/L	Se	100 mg/L
Co	100 mg/L	Tl	100 mg/L
Cu	100 mg/L	Ti	100 mg/L
Fe	100 mg/L	V	100 mg/L
Pb	100 mg/L	Zn	100 mg/L
Li	100 mg/L		

- INTER5 - Interference Check Standard 5: Spex Catalog #INTER5-100 (Inter 5): EM Science Catalog #EP20075-1

Al	1200 mg/L	Mg	3000 mg/L
Ca	6000 mg/L	Na	1000 mg/L
Fe	5000 mg/L		

- Alternate Metals III: Spex Catalog # MN-4-500

Ca	500 mg/L	K	100 mg/L
Na	500 mg/L	Mg	100 mg/L

- Alternate Metals II: CPI P/N 4400-010123

Ca	500 mg/L	K	100 mg/L
Na	500 mg/L	Mg	100 mg/L

- Alk. Stock Metals (PE Optima 4300 DV ICP)
    - Ca (Spex)- 500 mg/L (5 mL of 10,000 mg/L Standard mentioned diluted to 100 mL)
    - Na (Alfa)- 500 mg/L (5 mL of 10,000 mg/L Standard mentioned diluted to 100 mL)
    - K (Spex)- 100 mg/L (1 mL of 10,000 mg/L Standard mentioned diluted to 100 mL)
    - Mg (Spex)- 100 mg/L (1 mL of 10,000 mg/L Standard mentioned diluted to 100 mL)

Table 4a: Preparation of Solutions (TJA 61E Trace ICP)

Standard	Volume	Solution ID	Dilute w/ 6 % HNO_3, 5 % HCl to	Final Concentration
Standard 1	20 uL 2 mL	10,000 mg/L Si MIXSTD 1	200 mL	0.500 mg/L Be 1.50 mg/L Cd, Zn 5.00 mg/L Pb 1.00 mg/L Mn, Si 2.00 mg/L Se
Standard 2	2 mL	MIXSTD 2	200 mL	10mg/L Fe 1 mg/L Ba, Cu, Co, V
Standard 3	100 uL 100 uL 20 uL	10,000 mg/L As 10,000 mg/L Sn 10,000 mg/L Ti	200 mL	5.00 mg/L As 5.00 mg/l Sn 1.00 mg/L Ti
Standard 4	2.5 mL 0.5 mL	10,000 mg/L Ca 10,000 mg/L Al	250 mL	100 mg/L Ca 20 mg/L Al
Standard 5	2 mL 1.8 mL	MIX STD 5 10,000 mg/L Mg	200 mL	2.00 mg/L Sb, Tl 1.00 mg/L B 100.0 mg/L Mg 0.50 mg/L Ag
Standard 6 *	4 mL	QC-21	200 mL	1.0 mg/L Cr, Fe, Mo, Ni
ICV/CCV	5 mL 5 mL 0.5 mL 10 mL 225 uL 250 uL	QC-7 QC-21 10,000 mg/L Sn Alt. Metals III 10,000 mg/L Si 10,000 mg/L Tl	500 mL	See Table 5b
RLV1	5 mL	ICV	50 mL	See Table 5b
RLV2	1 mL	ICV	50 mL	See Table 5b
RLV3	0.5 mL	ICV	50 mL	See Table 5b
RLV4	0.25 mL	ICV	50 mL	See Table 5b
SIC 1	1.25 mL	10,000 mg/L Mo	500 mL	25 mg/L Mo
SIC 2	0.5 mL 0.5 mL 0.5 mL 0.5 mL 0.5 mL	10,000 mg/L Co 10,000 mg/L Cr 10,000 mg/L Cu 10,000 mg/L Mn 10,000 mg/L V	500 mL	10 mg/L Co 10 mg/L Cr 10 mg/L Cu 10 mg/L Mn 10 mg/L V
SIC 3	1.5 mL 5 mL 1 mL	10,000 mg/L Al 10,000 mg/L Fe 10,000 mg/L Ni	500 mL	30 mg/L Al 100 mg/L Fe 20 mg/L Ni
Multi Element (ME) Spike	5 mL 5 mL 5 mL 5 mL	10,000 ppm Si 10,000 ppm Sr 10,000 ppm Sn 10,000 ppm Tl	500 mL	100 ppm Si 100 ppm Sr 100 ppm Sn 100 ppm Tl
As Profile Solution	50 uL	10,000 mg/L As	500 mL	0.5 mg/L
Yttrium I.S.	0.1 mL	10,000 mg/L Y	200 mL	5 mg/L

Standard	Volume	Solution ID		Final Concentration
Digested LCS/MS (aqueous/nonaqueous)	0.5 mL 0.5 mL 2.0 mL 2.0 mL	QC-7 QC-21 Alt. Metals III ME Spike	Added to 50 mL of DI water/sample/1.5g diluted to 50 mL	See Table 5b
Undigested LCS/MS	50 uL 50 uL 200 uL 100 uL	QC-7 QC-21 Inter 5 10,000 mg/L Na	Added to 10 mL of sample (final volume 10.4 mL)	See Table 5b
Undigested LCS/MS (For Silicon/Silica or Tin Only)	1 mL	ME Spike	Added to 20 mL of sample (final volume 21 mL)	4.76 mg/L Si 4.76 mg/L Sr 4.76 mg/L Sn 4.76 mg/L Tl

Shelf Life of Solutions:

- 10,000 mg/L and 1000 mg/L Stock Solutions – One year from date opened or manufacturer's expiration date.
- Stock Solutions (50 mg/L or greater) – six months from date of preparation.
- Working Standards and ICVs – 1 month from date of preparation.
- Reporting Limit Verifications - 1 month from date of preparation.
- Spectral Interference Checks – 1 month from date of preparation.
- Arsenic Profile Solution – No expiration date.
- Yttrium IS – Prepare when needed

* Standard 6 also has a final concentration of 2 mg/L for As, Be, Ca, Cd, Co, Cu, Li, Mg, Mn, Pb, Sb, Se, Sr, Ti, Tl, V, Zn. However, these parameters are not used as calibration points on the instrument.

Table 4b Preparation of Solutions (PE Optima 4300 DV ICP)

Standard	Volume	Solution ID	Dilute w/ 6 % HNO_3, 5 % HCl to	Final Concentration
Cal Standard/CCV	10 mL 10 mL 50 mL 1.0 mL	QC-7 Env. Express QC-21 Env. Express Alt. Metals II CPI Sn 10,000 Alfa	1000 mL	See Table 5a
ICV	10 mL 10 mL 50 mL 1.0 mL	QC-7 Spex QC-21 Spex Alt Metals III- Spex Sn 10,000 – Spex	1000 mL	See Table 5a
RLV 1	1 mL	Cal Standard	10 mL	See Table 5a
RLV 2	0.2 mL	Cal Standard	10 mL	See Table 5a
RLV 3	0.05 mL	Cal Standard	10 mL	See Table 5a
RLV 4	0.5 mL	Cal Standard	10 mL	See Table 5a
SIC 1	1.25 mL	10,000 mg/L Mo	500 mL	25 mg/L Mo
SIC 2	0.5 mL 0.5 mL 0.5 mL 0.5 mL 0.5 mL	10,000 mg/L Co 10,000 mg/L Cr 10,000 mg/L Cu 10,000 mg/L Mn 10,000 mg/L V	500 mL	10 mg/L Co 10 mg/L Cr 10 mg/L Cu 10 mg/L Mn 10 mg/L V
SIC 3	1.5 mL 5 mL 1 mL	10,000 mg/L Al 10,000 mg/L Fe 10,000 mg/L Ni	500 mL	30 mg/L Al 100 mg/L Fe 20 mg/L Ni
Multi Element (ME) Spike	5 mL 5 mL 5 mL 5 mL	10,000 ppm Si 10,000 ppm Sr 10,000 ppm Sn 10,000 ppm Tl	500 mL	100 ppm Si 100 ppm Sr 100 ppm Sn 100 ppm Tl
Yttrium I.S.	1.50 mL	10,000 mg/L Y	250 mL	60 mg/L
Digested LCS/MS (aqueous/nonaqeous)	0.5 mL 0.5 mL 2.0 mL 2.0 mL	QC-7 QC-21 Alt. Metals III ME Spike	Added to 50 mL of DI water/sample/1.5g diluted to 50 mL	See Table 5a
Undigested LCS/MS	50 uL 50 uL 200 uL 100 uL	QC-7 QC-21 Inter-5 10,000 mg/L Na	Add to 10 mL of sample (final volume Is 10.4 mL)	See Table 5a
Undigested LCS/MS (For Tin Only)	1 mL	ME Spike	Added to 20 mL of sample (final volume 21 mL)	4.76 mg/L Si 4.76 mg/L Sr 4.76 mg/L Sn 4.76 mg/L Tl

Shelf Life of Solutions:

- 10,000 mg/L and 1000 mg/L Stock Solutions – One year from date opened or manufacturer's expiration date.
- Stock Solutions (50 mg/L or greater) – six months from date of preparation.
- Working Standards and ICVs – 1 month from date of preparation.
- Reporting Limit Verifications - 1 month from date of preparation.
- Spectral Interference Checks – 1 month from date of preparation.
- Copper Profile Solution – No expiration date.
- Yttrium IS – Prepare when needed

Table 5a Final Concentrations for PE Optima 4300 DV ICP

Element	ICV/CCV Conc. (mg/L)	RLV 1 Conc. (mg/L)	RLV 2 Conc. (mg/L)	RLV 3 Conc. (mg/L)	RLV 4 Conc. (mg/L)	Aqueous Digested LCS/MS Conc. (mg/L)	Nonaqueous Digested LCS/MS Conc. (mg/Kg)	Undigested LCS/MS Conc. (mg/L)
Aluminum	1.00	0.100	0.020	NA	0.050	1.00	33.3	23.5
Antimony	1.00	0.100	0.020	NA	0.050	1.00	33.3	0.48
Arsenic	1.00	0.100	0.020	NA	0.050	1.00	33.3	0.48
Barium	1.00	0.100	0.020	NA	0.050	1.00	33.3	0.48
Beryllium	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Boron	1.00	0.100	0.020	NA	0.050	1.00	33.3	0.48
Calcium	26.0	2.60	0.520	0.130	1.30	21.0	700	115
Cadmium	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Chromium	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Cobalt	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Copper	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Iron	1.00	0.100	0.020	NA	0.050	1.00	33.3	96.6
Lead	1.00	0.100	0.020	NA	0.050	1.00	33.3	0.48
Lithium	1.00	0.100	0.020	NA	0.050	1.00	33.3	0.48
Magnesium	6.00	0.60	0.120	0.030	0.30	5.0	167	58.2
Manganese	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Molybdenum	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Nickel	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Potassium	15.0	1.5	0.300	0.075	0.75	14.0	467	4.81
Selenium	1.00	0.100	0.020	NA	0.050	1.00	33.3	0.48
Silicon	NA	NA	NA	NA	NA	4.5	150	0.24
Silver	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Sodium	26.0	2.60	0.520	0.130	1.30	21.0	700	116
Strontium	1.00	0.100	0.020	NA	0.050	5.00	167	0.48
Thallium	1.00	0.100	0.020	NA	0.050	1.00	33.3	0.48
Tin	10.0	1.0	0.200	0.050	0.50	4.0	133	4.76
Titanium	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Vanadium	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48
Zinc	1.00	0.100	0.020	0.005	0.050	1.00	33.3	0.48

Table 5b Final Concentrations for TJA 61E Trace ICP

Element	ICV/CCV Conc. (mg/L)	RLV 1 Conc. (mg/L)	RLV 2 Conc. (mg/L)	RLV 3 Conc. (mg/L)	RLV 4 Conc. (mg/L)	Aqueous Digested LCS, MS Conc. (mg/L)	Nonaqueous Digested LCS/MS Conc. (mg/Kg)	Undigested LCS/MS Conc. (mg/L)
Aluminum	1.00	0.100	N/A	N/A	N/A	1.00	33.3	23.5
Antimony	1.00	0.100	0.020	0.01	N/A	1.00	33.3	0.48
Arsenic	1.00	0.100	0.020	0.01	N/A	1.00	33.3	0.48
Barium	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Beryllium	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Boron	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Calcium	11.0	1.1	0.22	0.11	0.055	21.0	700	115
Cadmium	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Chromium	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Cobalt	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Copper	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Iron	1.00	0.100	0.020	0.01	0.005	1.00	33.3	96.6
Lead	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Lithium	N/A	N/A	N/A	N/A	N/A	1.00	33.3	0.48
Magnesium	3.00	0.30	0.06	0.03	N/A	5.0	167	58.2
Manganese	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Molybdenum	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Nickel	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Potassium	N/A	N/A	N/A	N/A	N/A	14.0	467	4.81
Selenium	1.00	0.100	0.02	0.01	N/A	1.00	33.3	0.48
Silicon	5.0	0.50	0.1	0.05	0.025	4.5	150	4.76
Silver	1.00	0.100	0.020	0.01	0.005	1.00	33.3	0.48
Sodium	N/A	N/A	N/A	N/A	N/A	21.0	700	19.7
Strontium	N/A	N/A	N/A	N/A	N/A	5.00	167	0.48
Thallium	6.00	0.60	0.12	0.06	0.03	1.00	33.3	0.48
Tin	10.00	1.0	0.20	0.1	0.05	4.0	133	4.76
Titanium	1.00	0.1	0.020	0.01	0.005	1.00	33.3	0.48
Vanadium	1.00	0.1	0.020	0.01	0.005	1.00	33.3	0.48
Zinc	1.00	0.1	0.020	0.01	0.005	1.00	33.3	0.48

Title: Mercury

USEPA SW-846 7470A/7471A

Approvals (Signature/Date):

Keith Hutchison 5/22/08 Keith Hutchison Date Department Manager	Jason M. Lykins 5/22/08 Jason Lykins Date EH&S Officer
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This SOP was previously referenced as DT-MET-018 rev1.

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1.0 Scope & Application

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

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

1.3 This SOP has been approved by OVAP for the sample preparation and analysis of mercury in Soil Gas and Air samples. Reported results will be referenced as Modified USEPA SW-846 Method 7470A / 7471A / NIOSH 6009.

1.4 The current reporting limit for Mercury is 0.2 µg/L for aqueous samples, 0.00833 mg/Kg for nonaqueous samples, 0.005 ug/wipe for wipe samples, and 0.02 ug/sample for air samples. Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory-specific, method detection limit (MDL) data, project specific DQOs, regulatory requirement are all taken into account, as well as instrument-to-instrument repeatability.

1.5 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis as indicated in the QA Manual. **OVAP does not allow modifications to the SOP.**

2.0 Summary of Method

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

2.2 Methods 7470A and 7471A are both cold-vapor atomic absorption techniques that are based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

3.0 Definitions

ELEMENT- The Laboratory Information Management System

4.0 Interferences

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

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

4.3 Samples such as seawaters, brines, and industrial effluents high in chlorides require additional solid permanganate because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine hydrochloride.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) 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

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

This procedure could involve repetitive motions which could cause stress and an illness for the employee. Employee must avoid carrying out this task for extended periods of time or the work must be split up among the employees where possible.

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 standards 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.

Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 mg/M3 TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause

			deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, and productivity. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 Flow Injection Mercury System (FIMS-100): The FIMS-100 consists of an atomic absorption spectrometer designed to measure the absorption of mercury, a flow injection system to prepare the samples for the spectrometer, an autosampler, and a printer.

6.2 Hot Block / Hot Plate capable of maintaining temperatures of 90° to 95° C.

6.3 Environmental Express Disposable Digestion Cups – 50 mL with caps (the manufacturer Volume Certification for each lot is kept on file).

6.3.1 Equivalent disposable centrifuge tubes may also be used. If the manufacturer is not able to supply a volume certification, the laboratory must follow an established in-house volume certification/calibration check procedure.

6.4 Macropipettes and micropipettes with disposable tips.

6.5 Miscellaneous laboratory glassware and disposable plastic ware

6.6 Filter paper – Whatman No. 4 or 41 or equivalent

6.7 Maximum registering thermometer, or equivalent.

6.8 Analytical balance, with capability to measure to 0.1 mg, for use in weighing reagents and preparing standards.

6.9 Miscellaneous Glassware: All reusable labware must be sufficiently clean for the task objectives. Particular attention must be given to all ground glass surfaces during cleaning. Routinely all items should be soaked in 30% HNO_3 and rinsed 3 times in deionized water.

6.10 Disposable Digestion Vessel – 100 mL with flip top lids.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, or productivity. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

7.1 All standards/Reagents may be stored at room temperature.

7.2 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents must 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 questionable, analyze the reagent to determine the level of impurities.

7.3 The preparation amounts of all standards, reagents, and solutions may vary from those listed.

7.4 Reagent Water. Reagent water will be interference free. All references to water in this SOP refer to reagent water unless otherwise specified. The Metals Department uses Deionized Water as Reagent Water.

7.5 Nitric Acid (HNO_3), concentrated: Trace Metal grade or better. Shelf life is one year after opening or manufacturer expiration date (whichever is shorter).

7.6 Hydrochloric Acid (HCl), concentrated: Trace Metal grade or better. Self life is one year after opening or manufacturer expiration date (whichever is shorter).

7.7 Hydrochloric Acid (HCl), 3% FIMS Instrument Carrier Solution: Prepare by adding 90 mL of concentrated hydrochloric acid to approximately 1 L of deionized water and then dilute to 3 L with deionized water. Prepare fresh daily.

7.8 Sulfuric Acid (H_2SO_4), concentrated, assayed mercury level <1 µg/L.

7.9 Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCL to one volume of concentrated HNO_3. Allow mixing on stirplate on slow speed for a minimum of one hour before use. Otherwise excessive foaming will occur.

7.10 Mercury CCV/Calibration Stock Standard (1000 mg/L): purchased. The shelf life is the manufacturer's expiration date or 1 year after opening (whichever is shorter).

7.11 Mercury CCV/Calibration Working Standard (0.5 mg/L): Into a 100 mL volumetric flask, add the following:

7.11.1 Approximately 10 mL of deionized water

7.11.2 50 µL of Mercury CCV/Calibration Stock Standard (1000 mg/L)

7.11.3 1.0 mL HNO_3.

7.11.4 Dilute to 100 mL mark with deionized water. Mix well. Self life is one month after preparing or manufacturer expiration date (whichever is shorter).

7.12 Mercury ICV Stock Standard (1000 mg/L): This is a purchased standard that is from a different source than the Mercury CCV Stock Standard. The shelf life is the manufacturer's expiration date or 1 year after opening (whichever is shorter).

7.13 Mercury ICV Working Standard (0.5 mg/L): In a 100 mL volumetric flask, add the following:

7.13.1 Approximately 10 mL of deionized water

7.13.2 50 µL of Mercury ICV Stock Standard (1000 mg/L)

7.13.3 1.0 mL HNO_3.

7.13.4 Dilute to 100 mL mark with deionized water. Mix well. Self life is one month after preparing or manufacturer expiration date (whichever is shorter).

7.14 Calibration Standards and ICV: Prepare according to the directions in Tables 1 and 2.

7.15 Potassium Permanganate solution: Dissolve 100g of $KMnO_4$ in 2 L of deionized water. Shelf life: One month.

7.16 Potassium Persulfate solution: Dissolve 100g of $K_2S_2O_8$ in 2 L of deionized water. Shelf life: One month.

7.17 Sodium chloride-hydroxylamine hydrochloride solution ($NaCl$-NH_2OH-HCl): Dissolve 240g of $NH_2OH \cdot HCL$ and 240 g NaCl in 2 L deionized water. Mix well. Shelf life: One month.

7.18 Stannous chloride solution: Add 22 g of $SnCl_2$ and 60 mL of HCl and dilute to 2 L. Prepared daily.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples must be acidified to a pH of <2 with Nitric Acid. If sample pH >2, acid must be added and the sample verified to have a pH <2. If samples are found to be pH >2, then additional acid is added. The sample must be held for at least 24 hours after preservation, except drinking waters which must be held for at least 16 hours.

8.2 Nonaqueous samples/soils require refrigeration at <6.0°C, but not frozen, prior to analysis.

8.3 Mercury in Air is collected on Hopcalite sorbent tubes. Volume of air collected is directly related to the required detection limit. The larger the volume, the lower the detection limit. Generally between 10 – 200 L of air is collected. Samples are stored at ≤25°C. Holding time is 30 days from collection.

8.4 All standards and reagents used for this analysis are stored at room temperature.

8.5 Plastic and glass are both acceptable for sample storage.

8.6 The holding time is 28 days for aqueous/nonaqueous samples.

9.0 Quality Control

9.1 Each batch of 20 or fewer samples (aqueous & nonaqueous/wipe) or 10 or fewer samples (air) must contain:

- One Preparation Blank(PB)/Method Blank (MB or BLK)
- One Laboratory Control Sample (LCS)/Blank Spike (BS)
- One Matrix Spike (MS) / Matrix Spike Duplicate (MSD) pair (aqueous & nonaqueous soils only)
- One Duplicate (DUP) to be designated as a Post-Digestion Dilution (1+4) Test Sample.
- One Post Spike (PS) to be designated as a Post-Digestion Spike sample.
- For wipe and Air samples, batch Quality Control will consist of a PB/MB/BLK, LCS/BS, LCSD (Laboratory Control Sample Duplicate)/BSD (Blank Spike Duplicate), DUP, & PS
- For Air samples, the PB/MB/BLK, LCS/BS, and LCSD/BSD will be prepared using the Hopcalite sorbent and the front glass wool plug from an unused Hopcalite tube.

9.2 One Preparation Blank (PB) / Method Blank (MB or BLK). This will automatically be added by ELEMENT. This BLK is a deionized water blank that is carried through the digestion procedure and contains the same volumes of reagents as the sample solutions. The BLK will be useful in determining if samples are being contaminated.

9.2.1 Acceptance criteria is <RL. If the method blank shows a detection above the required reporting limit, it must be reanalyzed. If this fails to correct the problem, all associated samples with concentrations above the reporting limit must be re-digested.

- If the associated samples are non-detect, then reanalysis of the Method Blank is not required and re-digestion of samples is not required.
- If a sample cannot be re-digested and re-analyzed, the data will be reported with an appropriate data qualification flag.
- If the concentration found in the samples is >10X the concentration found in the Method Blank, reanalysis is not required, but data must be flagged. **This exception is not allowed by OVAP.**

9.2.2 When analyzing samples that get reported down to the MDL, if a value is greater than the MDL but less than the MRL, all samples with hits above the MDL will be reported as-is with an appropriate data qualification flag.

9.3 One Laboratory Control Sample (LCS) / Blank Spike (BS). This will automatically be added by ELEMENT. The LCS/BS is a blank that is spiked with a known concentration of metals and is carried through the same procedure as a sample would go through. The LCS/BS will be useful in determining accuracy by showing that a known concentration of metals can be taken through the procedure and recovered within the established acceptance limits. The current acceptance limits are located in the QA Manual. In order to evaluate wipe and air sample batch precision, a LCS/BS and LCSD/BSD will be prepared and analyzed.

9.3.1 If the LCS recovery is outside of the acceptance limits, it may be repeated one time.

9.3.2 If the LCS is still outside of the acceptance limits, all samples prepared with the LCS in the batch must be re-prepped/reanalyzed with the following exception:

- If the LCS recovery fails high for a specific parameter, associated samples in that batch are not required to be re-digested if there was no detection for that parameter in those samples.
- If no additional sample has been provided for re-digestion or if the holding times have been exceeded, then the data user should be provided with the sample results, the LCS results and a discussion of the corrective action undertaken by the laboratory.

9.4 One Matrix Spike (MS) / Matrix Spike Duplicate (MSD) pair. This will automatically be added by ELEMENT; however, the digestion technician must select which sample to use for this pre-digestion spike requirement. This selected sample will be digested three times: once non-spiked, once spiked as the MS, and once spiked as the MSD. The MS/MSD is spiked with a known concentration of metals. The MS/MSD will be useful in determining precision and bias. The current acceptance limits are located in the QA Manual. Due to the fact that the entire sample is digested for wipes and air samples, a MS/MSD can not be prepared and analyzed.

- If the MS/MSD recoveries are not within the acceptance limits, the MS/MSD results are flagged.
- MS/MSD is not used for batch control.

9.5 One Duplicate (DUP) to be designated as a Post-Digestion Dilution (1+4) Test Sample. This will automatically be added by ELEMENT; however, the instrumentation analyst will select which sample to use for this post-digestion procedure and will add a data qualification flag to indicate that it is a Post-Digestion Dilution (1+4) Test Sample rather than a duplicate digested sample.

9.5.1 If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high, an analysis of a fivefold (1+4) dilution must agree within +/- 10% of the original determination. If not, an interference effect must be suspected and the data will be reported with an appropriate data qualification flag. One dilution test must be performed for every 20 samples or less of each matrix in a batch. The Post Dilution Test will be made as follows:

- Into a plastic disposable autosampler tube add 2 mL of prepared sample.
- Dilute to the 10 mL mark using the 3% HCl FIMS Instrument Carrier Solution
- Mix sample well.

9.6 One Post Spike (PS) to be designated as a Post-Digestion Spike sample. This will automatically be added by ELEMENT; however, the instrumentation analyst will select which sample to use for this post-digestion procedure as well as document the appropriate spike solutions and amounts to be added.

9.6.1 The Post Spike is an analyte spike added to a portion of a prepared sample, or its dilution, that must be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. If the spike is not recovered within the specified limits, the data will be reported with an appropriate data qualification flag. Spiking information will be specified in ELEMENT so that recoveries can be calculated using the LIMS. Spike concentrations may be adjusted based upon the concentrations of metals present in the sample. Our standard Post digestion spike will be prepared as follows:

- Into a plastic disposable autosampler tube, added 10 mL of prepared sample or diluted sample if appropriate.
- Add 20 uL of Mercury CCV/Calibration Working Standard (0.5 mg/L)
- Mix sample well.

9.7 In addition to the required batch QC, Standard-Addition procedure may also be used. Standard Addition is typically used only upon client request.

10.0 PROCEDURE

10.1 Non-Aqueous and Wipe Sample Digestion

10.1.1 Weigh out 0.6g – 0.69g of untreated sample and place the sample in the bottom of an approved disposable digestion tube. For the Method Blank (MB/BLK) and Laboratory Control Sample (LCS) / Blank Spike (BS), do not add anything to the disposable digestion tube. For wipe samples, place the entire wipe into the disposable digestion tube (no weight is required).

10.1.2 Add 1.25 mL of Deionzed Water

10.1.3 To the Laboratory Control Sample (LCS) / Blank Spike (BS) and to the Matrix Spike (MS) and Matrix Spike Duplicate (MSD), add 100 uL of the CCV/Calibration Working Standard.

10.1.4 Add 1.25 mL of Aqua Regia.

10.1.5 Heat 2 minutes in the Hot Block at 95° C.

10.1.6 Cool and dilute to 25 mL with Deionized Water.

10.1.7 Add 3.75 mL potassium permanganate solution to each digestion tube..

10.1.8 Mix thoroughly and add additional dry crystals of potassium permanganate reagent, if necessary, until the purple color persists for at least 15 minutes.

10.1.9 Place the screw cap onto each digestion vessel and fully tighten. Then loosen the screw cap ½ turn in order to allow pressure to be released if the sample becomes reactive during the heating and digestion procedure.

10.1.10 Mix thoroughly and place in the Hot Block for 30 minutes at 95° C.

10.1.11 Take out of the Hot Block and allow to cool. (This is a good place to stop if the analysis is to be run at a later time.)

10.1.12 Any sample that did not retain the purple color after heating for 30 minutes must be re-prepped using additional dry crystals of potassium permanganate. Some extremely difficult samples may require a reduction of initial sample weight.

10.1.13 Add 1.5 mL of hydroxylamine hydrochloride to reduce the excess permanganate. This should be done in a hood, as chlorine gas could be evolved.

10.1.14 The analysis of the samples is ready to take place.

10.2 Aqueous Sample Digestion

10.2.1 Transfer 25 mL of sample (or an aliquot of sample diluted to 25 mL) into an approved disposable digestion tube. For the Method Blank (MB/BLK) and Laboratory Control Sample (LCS) / Blank Spike (BS) add 25 mL of Deionized Water to the disposable digestion tube.

10.2.2 To the Laboratory Control Sample (LCS) / Blank Spike (BS) and to the Matrix Spike (MS) and Matrix Spike Duplicate (MSD), add 50 uL of the CCV/Calibration Working Standard.

10.2.3 Add 1.25 mL of concentrated sulfuric acid and mix.

10.2.4 Add 0.62 mL of nitric acid and mix.

10.2.5 Add 3.75mL of 5% potassium permanganate solution to each tube. (NOTE: sewage samples may require additional permanganate dry crystals to be added).

10.2.6 Mix thoroughly and add additional dry crystals of potassium permanganate reagent, if necessary, until the purple color persists for at least 15 minutes.

10.2.7 Add 2 mL of potassium persulfate to each tube.

10.2.8 Place the screw cap onto each digestion vessel and fully tighten. Then loosen the screw cap ½ turn in order to allow pressure to be released if the sample becomes reactive during the heating and digestion procedure.

10.2.9 Mix thoroughly and place in the Hot Block for 2 hours at 95° C.

10.2.10 Take out of the Hot Block and allow to cool. (This is a good place to stop if the analysis is to be run at a later time.)

10.2.11 Any sample that did not retain the purple color after heating for 2 hours must be re-prepped using additional dry crystals of potassium permanganate. Some extremely difficult samples may require a reduction of initial sample volume (a dilution).

10.2.12 Add 1.5 mL of hydroxylamine hydrochloride to reduce the excess permanganate. This should be done under a hood as Chlorine gas could be evolved.

10.2.13 The analysis of the samples is ready to take place.

10.3 **Air Sample Digestion**

10.3.1 For Air samples transfer the entire Hopcalite sorbent and the front glass wool plug into an approved 50 mL digestion tube.

10.3.2 Add 2.5 ml concentrated HNO_3 followed by 2.5 mL concentrated HCl.

10.3.3 Allow the sample to stand for 1 hour or until the black Hopcalite sorbent is dissolved. The solution will turn dark brown and may contain undissolved material. Swirl every 30 minutes.

Note: the Hg must be in the oxidized state to avoid loss. For this reason the nitric acid must be added first.

10.3.4 Bring to 50 mL with DI water. Carefully transfer the contents of the 50 mL tube to a 100 mL flip top container. Add an additional 50 mL DI water to the tube, transfer that to the 100 mL flip top, for a final volume of 100 mL.

- Note that the 50 mL digestion tubes are calibrated but the 100 mL flip top tubes are not. Therefore, do not dilute to the 100 mL line on the large flip top tube.

10.3.5 The final solution (blue to blue green in color) contains 2.5% HNO_3 and 2.5 % HCl, and is analyzed for Hg with no additional dilution (except for samples containing high concentration of Hg.

10.3.6 Method blank- Prepare the method blank (reagent blank) from blank sorbent media. Prepare the method blank using the procedure in 10.3.1 -10.3.5 at the same time the samples are prepared. A minimum of one method blank per batch of 10 samples or less must be prepared.

10.3.7 Laboratory Control Standard- Prepare the LCS/BS and LCSD/BSD by spiking blank sorbent media with 400ul of the CCV/Calibration Working Standard (at or near the mid range of the calibration curve). Prepare the LCS sample using the procedure outlined in 10.3.1-10.3.5 at the same time the samples are prepared.

10.3.8 The client may submit media lot or field blanks with each job. These samples will be logged into ELEMENT as samples but identified as media lot or field blanks. The client may request that blank subtraction be used in the calculations of their sample results. Blank subtraction for OVAP is not acceptable.

10.4 **Calibration**

10.4.1 Prepare a calibration curve at least daily. Since we are utilizing inorganic mercury standards, the curve is not required to be digested.

10.4.2 A separate calibration curve must be prepared for Non-Aqueous samples, for aqueous samples, for Wipe samples, and for Air samples.

10.4.3 The curve consists of a calibration blank and a series of 5 calibration standards. Prepare as indicated in Table 1 & Sections 10.4.5, 10.4.6, and 10.4.7

10.4.4 Analyze the curve and plot corrected absorbency values against mg/L standard. The line that is generated must not be forced through the origin.

- There must be a standard at or below the Reporting Limit in the calibration curve.
- The correlation coefficient must be 0.995 or greater using all calibration standards. NOTE: The blank is not used in calculating the correlation coefficient.
- Please refer to the QA Manual regarding protocols for dropping points of the calibration curve.

10.4.5 For Non Aqueous and wipe calibration:

- For the calibration blank (ICB/CCB), calibration standards, ICV, and CCV, add 1.25 mL of Deionized Water, the appropriate amount of spike standards listed in Table 1, and 1.25 mL Aqua Regia before diluting to 25 mL with Deionized Water, then add all of the reagents listed above in the Non-Aqueous Sample Digestion section. However, these items are not required to be heated in the Hot Block at 95 ^{o} C.

10.4.6 For Aqueous calibration:

- For the calibration blank (ICB/CCB), calibration standards, ICV, and CCV, add the appropriate amount of spike standards listed in Table 1, dilute to 25 mL with Deionized Water, then add all of the reagents listed above in the Aqueous Sample Digestion section. However, these items are not required to be heated in the Hot Block at 95 ^{o} C.

10.4.7 For Air Sample calibration:

- For the calibration blank (ICB/CCB), calibration standards, ICV, and CCV, add the appropriate amount of spike standards listed in Table 1, 2.5 mL concentrated HNO_3, followed by 2.5 mL concentrated HCl before diluting to 50 mL with Deionized Water. Carefully transfer the contents of the 50 mL tube to a 100 mL flip top container. Add another 50 mL DI water to the tube and transfer that to the 100 mL flip top.

10.4.8 <u>Initial Calibration Verification Standard (ICV) / Continuing Calibration Verification Standard (CCV)</u>

- Analyze the ICV (secondary source) immediately following a calibration curve to verify the curve. The analysis of this ICV will also serve as the first bracketing Calibration Verification of the analytical sequence. In other words, instead of analyzing the <u>ICB-ICV-CCB-CCV-10 samples-CCB-CCV</u>, the sequence will be <u>ICB-ICV-10 samples-CCB-CCV</u>.

- The percent recovery acceptance criteria is +/- 10% of the true value. If the ICV fails, it may be repeated one time.
- If the repeated ICV passes, you may proceed with the analytical sequence.
- If the repeated ICV fails, the analytical sequence must be terminated and the problem investigated. First, verify that the ICV standard was prepared correctly. If the preparation is questionable, re-prepare the ICV standard and reanalyze. If the re-prepared ICV standard passes and it is determined that the first ICV standard was incorrectly prepared, the analytical sequence may proceed. If the re-prepared ICV standard also fails, further investigation is required. Verify that the calibration blank and standards were prepared correctly. Check the instrument autosampler tubing for clogged or poor connections. If any of these items are determined to be the cause of the problem, the items must be fixed. Since you may not be able to determine if this problem occurred before, during, or after the calibration, the entire analytical sequence, including the calibration and instrument QC check standards must be repeated.

10.4.9 Analyze the CCV (same source as Calibration Standard 4) after every 10th sample and at the end of the analytical sequence. The percent recovery acceptance criteria is ± 10% of the true value. If the CCV fails, it may be repeated one time.

- If the repeated CCV passes, you may proceed with the analytical sequence without repeating any sample analyses.
- If the repeated CCV fails, the analytical sequence must be terminated and the 10 samples prior to the failing CCV must be repeated once the problem has been investigated and fixed. Since this CCV standard is the same standard used for Calibration Standard 4, incorrect standard preparation would not be suspected. Therefore, check the instrument autosampler tubing for clogged or poor connections. If any of these items are determined to be the cause of the problem, the items must be fixed. After fixing these problems and analyzing a passing CCV, you must reanalyze the 10 samples prior to the failing CCV, but may continue with the analytical sequence without recalibrating. This is acceptable because you are able to determine that the isolated problem occurred between a passing CCV and a failing CCV.
- If after fixing the problem the CCV still fails, the instrument must be recalibrated and the analytical sequence repeated for any samples that were not bracketed by passing CCVs.

10.4.10 <u>Instrument Calibration Blank (ICB) / Continuing Calibration Blank (CCB)</u>

- Analyze the ICB immediately following a calibration curve to verify the curve. Analyze the CCB after every 10th sample and at the end of the analytical sequence.
- If a value is greater than the Method Reporting Limit (MRL), all samples between that CCB and the previous passing CCB must be re-analyzed for that failing parameter.
- When analyzing samples that get reported down to the MDL, if a value is greater than the MDL but less than the MRL, all samples with hits above the MDL will be reported as-is with an appropriate data qualification flag.

10.5 Sample Analysis

10.5.1 Set up instrument per manufacturer instructions.

10.5.2 The Stannous chloride and the 3% HCl FIMS Instrument Carrier Solution will be continuously added to the samples by the automated mixing coil incorporated into the FIMS instrument set-up.

10.5.3 Analyze the calibration curve in order of increasing concentration.

10.5.4 Evaluate the calibration to ensure that criteria in Section 10.4 are met.

10.5.5 Once an acceptable calibration curve has been achieved, proceed with analysis of samples and quality control samples using manufacturer's autosampler protocols.

10.5.6 Load the autosampler using the following sequence and follow all requirements listed in the Quality Control section of this SOP.

- A calibration blank plus 5 calibration standards
- Initial Calibration Blank (ICB)
- Initial Calibration Verification (ICV-2.00 ppb)
- Sample 1. Method Blank (BLK)
- Sample 2. Laboratory Control Sample (LCS) / Blank Spike (BS)
- Sample 3. Batch QC sample
- Sample 4. Matrix Spike (MS)
- Sample 5. Matrix Spike Duplicate (MSD)
- Samples 6-10
- Continuing Calibration Blank (CCB). Analyzed after every 10th sample and at the end of the sequence.
- Continuing Calibration Verification (CCV-5.00 ppb) Standard. Analyzed after every 10th sample and at the end of the sequence.
- Samples 11-20
- Continuing Calibration Verification (CCV-5.00 ppb) Standard.
- Continuing Calibration Blank (CCB)

11.0 Calculations / Data Reduction

11.1 All calculations for all analyses (standards and samples) are based on the average of two replicate instrument readings.

Results from instrument are in ug/L

11.2 Result of Mercury in mg/L:

Result (mg/L) = (Reading, ug/L) x (1000) (Dilution Factor)

11.3 Result of Mercury in ug/L:

Result (ug/L) = (Reading, ug/L) x (Dilution Factor)

11.4 Result of Mercury in mg/Kg:

$$\text{Result (mg/Kg)} = \frac{\text{(Reading, ug/L) x (Volume, mL) x (Dilution Factor)}}{\text{(Grams of sample) x 1000}}$$

11.5 Result of Mercury in ug/wipe (used for wipes):

$$\text{Result (ug/wipe)} = \frac{\text{(Reading, ug/L) x (Volume, mL) x (Dilution Factor)}}{\text{(1 wipe) x 1000}}$$

May also be reported as total micrograms

NOTE: Hg in wipes is not an OVAP certified parameter.

11.6 Result of Mercury in ug/sample (used for Air):

$$\text{Result (ug/sample)} = \frac{\text{(Reading, ug/L) x (Volume, mL) x (Dilution Factor)}}{\text{(1 sample) x 1000}}$$

May also be reported as total micrograms

Results will routinely be reported in ug/sample or total micrograms. Adjustments for air volume sampled, as in 11.7, will be performed per client request.

11.7 Result of Mercury in ug/m^3 (used for Air):

$$\text{Result (ug/m}^3\text{)} = \frac{\text{(ug/sample as in 11.6) - (ug/blank) x (Dilution Factor)}}{\text{Volume of air sampled (L)}}$$

NOTE: Report ug/tube, total microgram or ug/sample for lot blanks, trip blanks, field blanks and BS/MSD samples, as no air volume is collected for these.

11.8 Relative Percent Difference (RPD) between Duplicates:

$$\text{RPD} = \frac{(\text{Larger Value} - \text{Smaller Value}) \times 100}{(\text{Average of the Values})}$$

11.9 Spike Recovery of Laboratory Control Standards, Matrix Spikes, and Matrix Spike Duplicates:

$$\%\,\text{Recovery} = \frac{(\text{S} - \text{U}) \times 100)}{\text{T}}$$

Where:

S = Spiked result
U = Unspiked result (use 0 for LCS)
T = Spike True Concentration

ELEMENT will perform calculations when reporting results based on dry weight.

12.0 Method Performance

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study - A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

13.0 Waste Management and 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).

13.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in the Corporate Environmental Health & Safety Manual for "Waste Management and Pollution Prevention."

13.2 The following waste streams are produced when this method is carried out:

13.2.1 Acidic waste is neutralized and discharged into the sanitary sewer.

13.2.2 Hg Standards (1000 mg/L) are collected and disposed of through a Waste Handler.

14.0 References / Cross-References

14.1 USEPA SW-846,"Method 7470A: Mercury in Liquid Waste (Manual Cold-Vapor Technique)", Office of Solid Waste, Revision 1, September 1994.

14.2 USEPA SW-846,"Method 7471A: Mercury in Solid or Semisolid Waste (Manual Cold Vapor Technique)", Office of Solid Waste, Revision 1, September 1994.

14.3 "FIMS- Flow Injection Mercury/Hydride Analyses: Recommended Analytical conditions and General Information", Perkin-Elmer, September 1996.

14.4 "FIMS- Flow Injection Mercury System Software Guide", Perkin Elmer, July 1994.

14.5 "FIMS-Flow Injection Mercury System: Setting Up and Performing Analyses", Perkin Elmer, March 1994.

14.6 "AS-90 Autosampler for Atomic Spectroscopy: Installation, Maintenance and System Description", Perkin Elmer, April 1994.

14.7 NIOSH 6009, modified

14.8 "Standard Operating Procedure 1827 Rev. 2.0: Analysis of Mercury in Air with a Modified NIOSH 6009 Method", U.S. EPA Environmental Response Team, 5/13/99

15.0 Method Modifications

Item	Method	Modification
7.1	7470A	25 mL of sample is used instead of 100 mL for samples/standards

7.1	7470A	Hot block tubes and a heating block are used instead of BOD bottles and a water bath for the preparation of the samples.
7.3	7470A	Stannous chloride solution is acidified with Hydrochloric Acid per instrumentation instructions.
7.3	7470A	Stannous chloride solution and 3% Hydrochloric Acid is automatically introduced into each sample rather than manually added to the samples.
7.1	7471A	Hot block tubes and a heating block are used instead of BOD bottles and a water bath for the preparation of the samples.
7.1	7471A	0.6 g of well-mixed sample is measured as per method 7471B.
7.3	7471A	Stannous chloride solution is acidified with Hydrochloric Acid per instrumentation instructions.
7.4	7471A	Stannous chloride solution and 3% Hydrochloric Acid is automatically introduced into each sample rather than manually added to the samples.

16.0 Attachments

Table 1 Concentration of Standards

17.0 Revision History

17.1 Revision Dates

17.1.1 9/14/2007

17.1.2 4/8/2008

17.2 Changes from last revision

Revision Date	Item	Change from	Change to	Reason
5/23/08	1.4	… and 0.002 ug/sample for air …	… and 0.02 ug/sample for air …	Typographical correction
5/23/08	5.1	n/a	Added warning for potential repetitive motion injuries	To be compliant with EH&S policies.
5/23/08	9.1	Batch of 20 or fewer samples …..	…20 or fewer samples (aqueous & nonaqueous/wipe) or 10 or fewer samples (air)….	To clarify the number of samples contained in each type of batch
5/23/08	9.1	A Preparation Blank ….	One Preparation Blank …. One Laboratory Control sample …..	To clarify the number of PB and LCS required per batch
5/23/08	9.1	n/a	MS/MSD pair is only required for aqueous and nonaqueous (soil) batches	To clarify that MS/MSD pair is not required for wipe and air sample batches

Revision Date	Item	Change from	Change to	Reason
5/23/08	9.1	For Air samples, batch Quality Control will consist of a PB/MB/BLK, LCS/BS, LCSD (Laboratory Control Sample Duplicate)/BSD (Blank Spike Duplicate), & PS	For wipe and Air samples, batch Quality Control will consist of a PB/MB/BLK, LCS/BS, LCSD (Laboratory Control Sample Duplicate)/BSD (Blank Spike Duplicate), DUP, & PS	To clarify the batch QC requirements for wipe and air samples.
5/23/08	10.3.6	Method blank- Prepare the method blank (reagent blank) from blank sorbent media. Prepare the method blank using the procedure in 10.3.1 -10.3.5 at the same time the samples are prepared. A minimum of one method blank per batch of 20 samples or less must be prepared	Method blank- Prepare the method blank (reagent blank) from blank sorbent media. Prepare the method blank using the procedure in 10.3.1 -10.3.5 at the same time the samples are prepared. A minimum of one method blank per batch of 10 samples or less must be prepared	To clarify the number of samples contained in the batch.
5/23/08	10.5.6	n/a	Ending CCV added to the run sequence example	To clarify run sequence requirements

18.0 Contingencies

If for any reason a part of this SOP cannot be followed, seek the guidance of the Department Supervisor or Quality Assurance Department. Document all deviations on a Corrective Action Report and submit to the QA Department.

This is an OVAP approved SOP. All changes, other than formatting or spelling, made to this SOP must be approved by OVAP prior to implementation.

Table 1: Concentration of Standards

Standard	Amount	Of Solution	Diluted to	Concentration
CCV/Calibration Working Standard	50 µL	1000 mg/L CCV/Calibration Stock Standard	100 mL DI Water	0.50 mg/L
Calibration Standard 1	10 µL	CCV/Calibration Working Standard	25 mL DI Water	0.2 µg/L
Calibration Standard 2	50 µL	CCV/Calibration Working Standard	25 mL DI Water	1.0 µg/L
Calibration Standard 3	150 µL	CCV/Calibration Working Standard	25 mL DI Water	3.0 µg/L
Calibration Standard 4 (also used for CCV)	250 µL	CCV/Calibration Working Standard	25 mL DI Water	5.0 µg/L
Calibration Standard 5	500 µL	CCV/Calibration Working Standard	25 mL DI Water	10 µg/L
Air Samples Calibration Standard 1	40 µL	CCV/Calibration Working Standard	100 mL DI Water	0.2 µg/L
Air Samples Calibration Standard 2	200 µL	CCV/Calibration Working Standard	100 mL DI Water	1.0 µg/L
Air Samples Calibration Standard 3	600 µL	CCV/Calibration Working Standard	100 mL DI Water	3.0 µg/L
Air Samples Calibration Standard 4 (also used for CCV)	1000 µL	CCV/Calibration Working Standard	100 mL DI Water	5.0 µg/L
Air Samples Calibration Standard 5	2000 µL	CCV/Calibration Working Standard	100 mL DI Water	10 µg/L
ICV Working Standard	50 µL	1000 mg/L ICV Stock Standard	100 mL DI Water	0.50 mg/L
ICV	100 µL	ICV Working Standard	25 mL DI Water	2.0 µg/L
Air Samples ICV	400 µL	ICV Working Standard	100 mL DI Water	2.0 µg/L
LCS/BS (aqueous)	50 µL	CCV/Calibration Working Standard	25 mL DI Water	1.0 µg/L
LCS/BS (non-	100 µL	CCV/Calibration	25 mL DI	2.0 µg/L

Standard	Amount	Of Solution	Diluted to	Concentration
aqueous)		Working Standard	Water	
LCS/BS (Air Samples)	400 µL	CCV/Calibration Working Standard	100 mL DI Water	2.0 µg/L
MS/MSD (aqueous)	50 µL	CCV/Calibration Working Standard	25 mL sample	1.0 µg/L
MS/MSD (non-aqueous)	100 µL	CCV/Calibration Working Standard	0.6g sample diluted to 25 mL with DI Water	2.0 µg/L (0.0833 mg/Kg)

Title: ICPMS Total Metals Sample Preparation (aqueous)

SW-846 Method 3010A

Approvals (Signature/Date):

Keith Hutchison — 12/8/09 Keith Hutchison — Date Department Manager	Jason Lykins — 12/8/09 Jason Lykins — Date EH&S Officer
Violet Fanning — 11/27/09 Violet Fanning — Date Quality Assurance Manager	Deborah Lowe — 12/8/09 Deborah Lowe — Date Laboratory Director

This SOP was previously referenced as DT-MET-019.0

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1.0 Scope and Application

1.1 This procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis by inductively coupled argon plasma-mass spectrometry (ICP-MS). See Table 2 for elements that may be digested using this procedure. This digestion is required for the determination of total metals.

1.2 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case as indicated in the QA Manual. **OVAP does not allow modifications to the SOP.**

2.0 Summary of Method

2.1 An aliquot of well-mixed, homogeneous aqueous sample is accurately measured for sample processing. For total metals analysis of an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After allowing to cool, the sample is poured up to volume, mixed and allowed to settle prior to analysis. If the sample should go to dryness, it must be discarded and the sample reprepared.

2.2 The method describes the procedures required to properly prepare aqueous samples for NPDES or RCRA metals analysis by ICP-MS.

3.0 Definitions

3.1 Total Recoverable - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid. Please see the ICP-MS Total Recoverable Metals Digestion SOP (DT-MET-003) for additional information about this digestion.

3.2 Total – The concentration determined on an unfiltered sample following vigorous digestion.

3.3 Element- The Laboratory Information Management System.

4.0 Interferences

4.1 Interferences are discussed in the referring analytical method.

4.2 Boron and silica from the glassware will leach into the sample solution during and following sample processing, therefore, PTFE plastic labware is used.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and 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

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

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
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

- Hot Block / Mod Block / Hot Plate capable of maintaining temperatures of 90° to 95° C.
- Environmental Express Disposable Digestion Cups – 50 mL with caps (the manufacturer Volume Certification for each lot is kept on file).
- Sample tubes, hinged caps, 70 mL Labware is verified initernally if used for volumetric purposes and not accompanied by a certificate
- Macropipettes and micropipettes with disposable tips.
- Miscellaneous laboratory glassware and disposable plastic ware.
- Filter paper – Whatman No. 4 or equivalent (optional).
- Thermometer that has been calibrated against a NIST traceable thermometer.

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, productivity, or cost. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

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 questionable, analyze the reagent to determine the level of impurities.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

All standards/reagents are stored at room temperature.

7.1 **Reagent Water**. Reagent water will be interference free. All references to water in this SOP refer to reagent water unless otherwise specified. The Metals Department uses Deionized Water as Reagent Water.

7.2 **Nitric Acid (HNO_3), Concentrated:** Trace Metal grade or better. Shelf life is one year after opening or manufacturer's expiration date (whichever is shorter).

7.3 **Nitric Acid (HNO_3), 1:1 Dilution:** Prepare by adding a volume of Concentrated acid to an equal volume of deionized water. Shelf life is one year after preparation or manufacturer expiration date (whichever is shorter).

7.4 **Hydrochloric Acid (HCl), Concentrated:** Trace Metal grade or better. Self life is one year after opening or manufacturer's expiration date (whichever is shorter).

7.5 **Hydrochloric Acid (HCl), 1:1 Dilution:** Prepare by adding a volume of Concentrated acid to an equal volume of Deionized water. Shelf life is one year after preparation or manufacturer expiration date (whichever is shorter).

7.6 **NET-MSICV-1 stock standard from Inorganic Ventures:** (20 ug/mL Al, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Ag, Se, Th, Tl, U, V, and Zn)

7.7 **NET-MSICV-2 stock standard from Inorganic Ventures:** (20 ug/mL Sb and Mo)

7.8 **Strontium stock standard:** (10,000 ug/mL Sr)

7.9 **Titanium stock standard:** (10,000 ug/mL Ti)

7.10 **ICP-MS ICV Stock 1:** prepare fresh monthly. Into a 50 mL Environmental Express Disosable Digestion Cup (or volumetric), add the following:

- 100 uL of Strontium stock standard, 10,000 ug/mL
- 100 uL of Titanium stock standard, 10,000 ug/mL
- 1.0 mL of concentrated Nitric Acid (HNO_3)
- Dilute to 50 mL mark with deionized water and mix well

7.11 **ICP-MS LCS/BS/MS/MSD Spike Working Solution**:, prepare fresh daily. Into a 50 mL Environmental Express Disposable Digestion Cup, add the following:

- Approximately 10 mL of deionzed water.
- 1.0 mL of 1:1 Nitric Acid (HNO_3)
- 2.5 mL of NET-MSICV-1

- 2.5 mL of NET-MSICV-2
- 2.5 ml of ICV Stock 1 (optional if Sr or Ti are needed)
- Dilute to 50 mL mark and mix well

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	Plastic or glass	250 mL	pH <2 with HNO_3, chill to <6.0°C but not frozen.	180 days from sampling to analysis	40 CFR Part 136

8.2 All aqueous metals samples (except Cr VI) must be acidified to a pH <2 with nitric acid upon collection or as soon as received at the lab. Samples are collected in pre-preserved sample containers. Proper preservation (pH <2) is checked prior to digestion. The pH is documented on the sample bottle cap, by a red or black line, and on the ICP-MS Preparation bench sheet.

8.3 If samples are found to be pH >2, then additional acid is added. If the sample pH >2 , the acid lot number, amount of acid, the date and time the acid was added are recorded on the sample cap or bottle and on the ICP-MS Preparation bench sheet. The sample must be held for at least 24 hours from the time indicated on the sample cap before the pH is check again. If the sample pH is still >2 then the sample must be flagged with the appropriate qualifier or additional acid added and held for an additional 24 hours then check the pH again before proceeding with preparation.

8.4 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus, which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorbtion and (b) by depleting concentrations through adsorption, thus the collection and treatment of the sample prior to analysis requires particular attention. The quality control program must document through the use of spikes sample, reagent and sample blanks, that cleaning procedures are adequate. Care must be taken to verity the fact that the containers in which acid digested samples, blanks, and standards are packaged do not contribute contaminants.

8.5 Before collection of the sample, a decision must be made as to the type of data desired, i.e., dissolved, suspended, or total.

9.0 Quality Control

9.1 The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency
Method Blank (MB)	1 per preparation batch[1]
Laboratory Control Sample (LCS)	1 per preparation batch[1]
Matrix Spike/Matrix Spike Duplicate (MS/MSD)[2]	1 per preparation batch[1]
Duplicate (DUP)[2]	1 per preparation batch[1]
Post Spike [2]	1 per preparation batch[1]

[1]Preparation batch is limited to 20 samples
[2]The sample selection for MS/MSD/DUP and Post Spike is random, unless specifically requested by a client.

9.2 Batching samples using ELEMENT

Each batch of 20 or fewer samples must contain the following:

9.2.1 One Preparation Blank (PB) / Method Blank (MB or BLK). This will automatically be added by ELEMENT. This BLK is a Deionized water blank that is carried through the digestion procedure and contains the same volumes of reagents as the sample solutions. The BLK will be useful in determining if samples are being contaminated.

9.2.2 One Laboratory Control Sample (LCS) / Blank Spike (BS). This will automatically be added by ELEMENT. The LCS/BS is a blank that is spiked with a known concentration of metals and is carried through the same procedure as a sample would go through. The LCS/BS will be useful in determining accuracy by showing that a known concentration of metals can be taken through the procedure and recovered within the established acceptance limits.

9.2.3 One Matrix Spike (MS) / Matrix Spike Duplicate (MSD) pair. This will automatically be added by ELEMENT; however, the digestion technician must select which sample to use for this pre-digestion spike requirement. This selected sample will be digested three times: once non-spiked, once spiked as the MS, and once spiked as the MSD. The MS/MSD is spiked with a known concentration of metals. The MS/MSD will be useful in determining precision and bias.

9.2.4 One Duplicate (DUP) to be designated as a Post-Digestion Dilution (1+ 4) Test Sample. This will automatically be added by ELEMENT; however, the instrumentation analyst will select which sample to use for this post-digestion procedure and will add a data qualification flag to indicate that it is a Post-Digestion Dilution (1+ 4) Test Sample rather than a duplicate digested sample.

9.2.5 One Post Spike (PS) to be designated as a Post-Digestion Spike sample. This will automatically be added by ELEMENT; however, the instrumentation analyst will select which sample to use for this post-digestion procedure as well as document the appropriate spike solutions and amounts to be added.

10.0 Procedure

10.1 Transfer 50 mL of well-mixed sample into an approved digestion vessel.

Note: Sample volumes can be changed provided the volumes of reagents/standards used are adjusted proportionally.

10.1.1 For the Preparation Blank (PB) / Method Blank (MB or BLK) and the Laboratory Control Sample (LCS) / Blank Spike (BS), add 50 mL of Deionized water.

10.1.2 To the Laboratory Control Sample (LCS) / Blank Spike (BS) and to the Matrix Spike (MS) and Matrix Spike Duplicate (MSD) vessels, add 2.5 mL of the ICP-MS LCS/BS/MS/MSD Spike Working Solution.

10.1.3 Add 1 mL of 1:1 Nitric Acid to each digestion vessel.

10.1.4 In the Hot Block, evaporate samples to near dryness (about 5-10 mLs). Do not boil or allow samples to go dry.

Note: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment.

10.1.5 Allow samples to cool and add 1 additional mL of 1:1 Nitric Acid. Cover the tubes with the hinged cap or watchglass and gently reflux. Evaporate to near dryness (5-10ml), remove from heat, and allow to cool.

10.1.6 Continue heating, adding additional acid as necessary until digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).

10.1.7 Add 1 mL of 1:1 Hydrochloric acid and warm the digestion tubes to dissolve any precipitate or residue resulting from evaporation.

10.1.8 Remove the samples from the hot plate/block and allow to cool. Bring up to 50 mL with deionized water in the calibrated digestion vessels and mix well. At the discretion and preference of the instrumentation analysts, particulates in the digestate can then be removed by filtration, by centrifugation, or by allowing the sample to settle.

10.1.9 In ELEMENT, be sure to properly document the source and the amount of all standards, acids, and reagents used; the initial and final volumes of each sample; the temperature reading from the thermometer; and the date & time the digestion procedure was performed.

11.0 Calculations / Data Reduction - None Applicable.

12.0 Method Performance

The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.1 **Demonstration of Capabilities** - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.2 **Method Detection Limit Study** - A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

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). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

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 accordance with all federal and state laws and regulations. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Dayton's facility addendum.

14.1 The following waste streams are produced when this method is carried out:

- Acidic waste containing nitric & hydrochloric acids is neutralized and discharged into the sanitary sewer.
- Contaminated disposable materials utilized for the analysis is disposed of in the general trash.

15.0 References / Cross-References

15.1 Metals (Atomic Absorption Methods), "Methods for Chemical Analysis of Water and Wastes", Revised March 1983 and 1979.
15.2 Users Manual for Perkin Elmer ELAN 6000.
15.3 Method 200.8 using the ELAN 6000 ICP-MS, Perkin Elmer, Revision 2.0, 9/6/95 Draft.
15.4 SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", 3rd Edition, Method referenced 3010A.
15.5 DT-QAM-001 Quality Assurance Manual for TestAmerica Dayton
15.6 DT-QA-005 Procedure for Balance Calibration Check
15.7 DT-QA-006 Thermometer Calibration
15.8 DT-QA-007 Use and Calibration Verification of Pipets and Dispensing Apparatus.
15.9 DT-MET-003 ICPMS Total Recoverable Metals Sample Preparation (aqueous)
15.10 This is an OVAP approved SOP. All changes must be approved by OVAP prior to implementation.

16.0 Method Modifications:

Modifications:

Item	Method	Modification
4.2	3010A	Plastic labware is used to reduce the amount of potential contamination.
4.6	3010A	Temperature setting based on manufacturer's requirements.
5.3	3010A	1 mL of 1:1 Nitric Acid is used for the digestion step; 1 mL of 1:1 Nitric Acid is added for the reflux step
7.1; 7.2	3010A	1 mL of 1:1 Nitric Acid is used for the digestion step; 1 mL of 1:1 Nitric Acid is added for the reflux step
7.1	3010A	50 mL of well mixed sample is used instead of 100 mL
7.2	3010A	1 mL of 1:1 Hydrochloric Acid is used to dissolve excess precipitate.

17.0 Attachments

Table 1 Premixed Standard Concentrations:
Table 2 LCS, MS, and MSD Spike Concentrations:

18.0 Revision History

18.1 Revision dates

- 8/24/2007
- 12/8/2009- Biannual update

18.2 Changes from last revision

Revision Date	Item	Change from	Change to	Reason
12/8/09	title	ICPMS Total Metals Sample Preparation (aqueous) EPA Method 200.8 / SW-846 Method 3010A	Total Metals Sample Preparation (aqueous) SW-846 Method 3010A	Removed reference to EPA Method 200.8
12/8/09	Copyright	2007 information	2009 information	Update copyright and signatures
12/8/09	Section 6.0	Hot Block / Hot Plate	Hot Block / Mod Block / Hot Plate	Mod Block added as an option
12/8/09	Section 6.0	CPI Mod Block Vessels-Sample tubes	Sample tubes	Removed CPI Mod block Vessels, eliminate vendor specific item
12/8/09	Section 6.0	P/N 4370-010020 (the manufacture Volume Certificate of Compliance is kept on file)	Labware is verified internally if used for volumetric purposes and not accompanied by a certificate.	Remove vendor specific item and include internal labware verification
12/8/09	Section 6.0	Maximum registering thermometer	Thermometer that has been calibrated against a NIST traceable thermometer	Removed maximum registering thermometer and added calibration requirement.
12/8/09	Section 7.6 & 7.7	20 ug/L	20 ug/mL	Correct units of concentration
12/8/09	Section 7.8		Strontium stock standard	Additional optional element added
12/8/09	Section 7.9		Titanium stock standard	Additional optional element added
12/8/09	Section 7.10		ICP-MS ICV Stock 1	Additional optional elements added
12/8/09	Section 7.11	Addition of the optional elements was not there	Added 2.5 ml of ICV Stock 1 (optional if Sr or Ti are needed)	Additional optional elements added
12/8/09	Section 8, Section 9	Paragraph form	Table form	Ease of use and consistency with other SOPs
12/8/09	Section 8.2	All aqueous metals	All aqueous metals	Statements added to clarify

Revision Date	Item	Change from	Change to	Reason
		samples (except Cr VI) must be acidified to a pH <2 with nitric acid upon collection. Samples are preserved with 25% HNO_3 (8 mL of acid per Liter) at the time of collection. Proper preservation (pH <2) is checked prior to digestion. This is documented in the ICP Preparation Log.	samples (except Cr VI) must be acidified to a pH <2 with nitric acid upon collection or as soon as received at the lab. Samples are collected in pre-preserved sample containers. Proper preservation (pH <2) is checked prior to digestion. The pH is documented on the sample bottle cap, by a red or black line, and on the ICP-MS Preparation bench sheet.	sample collection, preservation and pH documentation.
12/8/09	Section 8.3	If samples are found to be pH >2, then additional acid is added. The sample must be held for at least 24 hours after preservation, except drinking waters which must be held for at least 16 hours.	If samples are found to be pH >2, then additional acid is added. If the sample pH >2 , the acid lot number, amount of acid, the date and time the acid was added are recorded on the sample cap or bottle and on the ICP-MS Preparation bench sheet. The sample must be held for at least 24 hours from the time indicated on the sample cap before the pH is check again. If the sample pH is still >2 then the sample must be flagged with the appropriate qualifier or additional acid added and held for an additional 24 hours then check the pH again before proceeding with preparation.	Statements added to clarify sample collection, preservation and pH documentation.
12/8/09	Section 10.1.4	(about 3-5 ml)	(about 5-10 ml)	Correct volume
12/8/09	Section 10.1.9	Maximum registering thermometer	thermometer	Remove maximum registering
12/8/09	Section 7 and tables	No information for Sr and Ti standards	Included information for the use of the Sr and Ti standards	To include Sr and Ti in the LCS, MS & MSD

Revision Date	Item	Change from	Change to	Reason
12/8/09	Section 19	Present	Removed	Information is present in other areas of SOP, and for consistency with other VAP SOPs.

Table 1 Premixed Standard Concentrations:

Premixed Standard Concentrations	
NET-MSICV-2	Sb, Mo at 20 mg/L
NET-MSICV-1	Al, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Ag, Se, Th, Tl, U, V, and Zn at 20 mg/L each
ICPMS ICV Stock I	Sr and Ti at 20 mg/L each

Table 2 LCS, MS, and MSD Spike Concentrations:

NET-MSICV-2			
Element	Original Standard	Spiking Solution, µg/mL	Final Conc., µg/L
Sb	20 µg/mL	1.0	50
Mo	20 µg/mL	1.0	50

NET-MSICV-1			
Element	Original Standard	Spiking Solution, µg/mL	Final Conc., µg/L
Al	20 µg/mL	1.0	50
As	20 µg/mL	1.0	50
Ba	20 µg/mL	1.0	50
Be	20 µg/mL	1.0	50
Cd	20 µg/mL	1.0	50
Cr	20 µg/mL	1.0	50
Co	20 µg/mL	1.0	50
Cu	20 µg/mL	1.0	50
Pb	20 µg/mL	1.0	50
Mn	20 µg/mL	1.0	50
Ni	20 µg/mL	1.0	50
Se	20 µg/mL	1.0	50
Ag	20 µg/mL	1.0	50
Tl	20 µg/mL	1.0	50
U	20 µg/mL	1.0	50
V	20 µg/mL	1.0	50
Zn	20 µg/mL	1.0	50

ICPMS ICV Stock I			
Sr	20 µg/mL	1.0	50
Ti	20 µg/mL	1.0	50

Title: Metals by ICP-MS
USEPA SW-846 6020A

Approvals (Signature/Date):

Jason Lykins — 8/29/07 — Date Department Manager / Supervisor	Jan Grover — 8/29/07 — Date Health & Safety Manager / Coordinator
Violet Fanning — 8/29/07 — Date Quality Assurance Manager	Deborah Lowe — 8/29/07 — Date Laboratory Director

There is no previous reference for this SOP. This version is the Original.

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1.0 Scope & Application

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water, waste and soil samples, extracts or digests. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. However, digestion is recommended to remove carbon interference when analyzing for chromium as well as to add enough HCl for stability of silver and antimony. Acid-digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludge, sediments, and other solid wastes for which total (acid-leachable) elements are required.

1.2 The following analytes can be determined by this procedure:

Analyte	Symbol	CAS #
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Iron	Fe	7439-89-6
Copper	Cu	7440-50-8
Magnesium	Mg	7439-95-4
Lead	Pb	7439-92-1
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Mercury	Hg	7439-97-6
Nickel	Ni	7440-02-0
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Thallium	Tl	7440-28-0
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

1.3 Please see the Quality Assurance Manual for current reporting limits. Reporting limits can be affected by sample volumes, matrix effects, dilutions and other factors and are therefore subject to change. Laboratory-specific, method detection limit (MDL) data, project specific DQOs, regulatory requirement are all taken into account, as well as instrument-to instrument repeatability.

1.4 On occasion clients may request slight modifications to this SOP. These modifications are addressed on a case by case basis with the supporting demonstration of sensitivity and accuracy (e.g. MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into project special instructions (e.g. Quality Assurance Project Plans), authorized by the laboratory, and mentioned in the report narrative. **OVAP does not allow modifications to the SOP.**

2.0 Summary of Method

2.1 Prior to analysis, samples that require total ("acid-leachable") values must be digested using appropriate sample preparation methods.

2.2 The method describes the multi-element determination of trace elements by ICP-MS. Sample material in solution is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1.0 amu peak width at 10% peak height. The ions transmitted through the quadrupole are detected by an electron multiplier and the ion information processed by a data handling system. Interference related to this technique must be recognized and corrected for. Such correction must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by sample matrix must be corrected for by use of internal standards.

3.0 Definitions

ELEMENT- The Laboratory Information Management System

4.0 Interferences

4.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, analysis using another verified and documented isotope or use of another method. See Table 1.

4.2 Isobaric molecular and doubly charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature Examples including $ArCl^+$ ions on the ^{75}As signal and MoO^+ on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature, the most precise coefficients for an

instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^{+}$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^{+}$ signal):

Corrected arsenic signal (using natural isotopes abundances for coefficient approximations) =

(m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z),

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^{+}$, (e.g., $^{81}BrH^{+}$ from bromine wastes).

Similarly,

Corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =

(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^{+} contributions at m/z 114).

NOTE: Cadmium values will be biased low by this type of equation when $^{92}Zr0^{+}$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH(+)$ and indirect ($^{90}ZrO(+)$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are ONLY illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. This type of correction has been reported for oxide-ion corrections using ThO^{+}/Th^{+} for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas has been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

4.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix

changes. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration (or in the case of the ELAN DRCe software, the calibration blank), the sample must be reanalyzed after a fivefold (1+4) dilution has been performed.

4.4 Memory interferences can occur when there are large concentration differences between samples or standards that are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affects the extent of the memory interferences that are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

4.5 If there is poor relative standard deviation (precision) on standards and sample:

4.5.1 Check that the interface cones are in good condition and that the orifices of both cones are round and of the proper size.

4.5.2 Evaluate the nebulizer to see if it is operating properly by checking the aerosol with the plasma off and the spray chamber removed. If the aerosol is not forming properly clean or replace the gem tips.

4.5.3 Check that the peristaltic pump tubing is in good condition. Follow air bubbles through the tubing to insure that the flow is smooth and not pulsating.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and 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

The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

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
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
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

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, and productivity. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met.

6.1 An ICPMS System capable of providing resolution, better than or equal to 1.0 amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. A mass-flow controller for the nebulizer argon and a peristalic pump for ample solution are recommended.

6.2 Argon gas supply: high-purity grade (99.99%).

6.3 Macropipettes and micropipettes with disposable tips.

6.4 Miscellaneous laboratory glassware and disposable plastic ware: All glassware and disposable plastic ware should be rinsed with dilute nitric acid and then rinsed three times with deionized water. The concentration of the nitric acid should be at least 10%. All ICP-MS glassware and disposable plastic ware is segregated from other glassware to help eliminate contamination.

6.5 Analytical Balance capable of weighing to the nearest 0.1 mg.

6.6 Autosampler tubes with caps.

6.7 Environmental Express Disposable Digestion Cups – 50 mL with caps (the manufacturer Volume Certification for each lot is kept on file).

6.8 CPI Mod Block Vessels – Sample tubes, hinged caps, 70 mL P/N 4370-010020 (the manufacturer Volume Certificate of Compliance is kept on file).

7.0 Reagents and Standards

The following items are recommended for performing this procedure. Equivalent items should only be used when they result in an improvement in quality, efficiency, or productivity. An item can be considered equivalent if with its use, the analytical and QA/QC requirements in this SOP can be met. Please refer to the MSDS prior to the use of any reagent or standard.

If alternate vendors are used, if the vendor changes the product or if the laboratory makes a procedural change, standard and reagents concentrations may change. If concentrations change, then the volumes used to prepare these must change accordingly.

All standards/Reagents may be stored at room temperature.

7.1 Acids used in the preparation of standards and for sample processing musts be of high purity. Nitric acid at less than 2 per cent (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used. Concentrations of antimony and silver between 50-500 ug/L require 1% (v/v) HCl for stability; for concentrations above 500 ug/L Ag, additional HCl will be needed.

7.2 Deionized Water.

7.3 Nitric Acid, concentrated: Trace Metal Grade or better.

7.4 Hydrochloric Acid (concentrated): Trace Metal Grade or better.

7.5 1:1 HNO_3 and 1:1 HCl acid: prepare 1:1 dilutions with deionized water by adding the concentrated acid to an equal volume of water.

7.6 Gases: Gases must be of high purity. Argon must be high purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional tanks.

7.7 Premixed commercially available Stock Solutions or equivalent. See Table 2 for a listing.

7.8 10,000 and 1,000 mg/L single element stock solutions.

7.9 Tuning Solution 1 stock standard from Spex (10 μg/L Be, Mg, Co, Rh, In, Ba, Ce, Pb, Li, Tl, U, and Y).

7.10 Tuning Solution 1 – working standard. Into a 500 mL volumetric flask, add the following:

- Approximately 50 mL of deionized water
- 1 mL of concentrated nitric acid
- 0.5 mL of Tuning Solution 1 – stock standard from Spex
- Dilute to the 500 mL mark with deionized water

7.11 6020ISS stock standard from Inorganic Ventures. See Table 2 for the concentrations.

7.12 Recommended internal standards include Li 6, Sc 45, Y 89, Rh 103, In 115, Tb 159, Ho 169 and Bi 209.

7.13 Gold stock standard (1,000 mg/L) from Inorganic Ventures (CGAUN1-1).

7.14 Germanium stock standard (10,000 mg/L) from Alfa Aesar.

7.15 Internal Standard Working Solution: Into a 50 mL Environmental Express digestion cup, add the following:

- 40 mL of 6020ISS stock standard from Inorganic Ventures
- 0.3 mL of Germanium stock standard (10,000 mg/L) from Alfa Aesar
- 1.2 mL of Gold stock standard (1,000 mg/L) from Inorganic Ventures

7.16 For Internal Standard Stock Solution and Sample concentrations see Table 2. Note that the concentrations of the Internal Standard Working Solution are based on a final volume of 41.5 mL.

7.17 ICSA stock standard from Inorganic Ventures (6020ICS-8A): See Table 2 for the concentrations

7.18 ICSA working standard. Into a 50 mL volumetric flask, add the following:

- Approximately 10 mL of deionized water
- 1 mL of concentrated nitric acid
- 0.5 mL of concentrated hydrochloric acid
- 0.5 mL of ICSA stock standard from Inorganic Ventures (6020ICS-8A)
- 200 uL of Internal Standard Working Solution
- Dilute to the 50 mL mark with deionized water

7.19 2008CAL-1 stock standard from Inorganic Ventures: See Table 2 for the concentrations.

7.20 2008CAL-2 stock standard from Inorganic Ventures: See Table 2 for the concentrations.

7.21 ICSAB working standard: Into a 50 mL volumetric flask, add the following:

- Approximately10 mL of deionized water
- 1 mL of concentrated nitric acid
- 0.5 mL of concentrated hydrochloric acid
- 0.5 mL of ICSA stock standard from Inorganic Ventures (6020ICS-8A)
- 50 uL of 2008CAL-1 stock standard from Inorganic Ventures
- 50 uL of 2008CAL-2 stock standard from Inorganic Ventures
- 200 uL of Internal Standard Working Solution
- Dilute to the 50 mL mark with deionized water

7.22 Calibration Standard 1: For final concentrations and premixed standard concentrations, see Table 2. Into a 100 mL volumetric flask, add the following:

- Approximately 10 mL of deionized water.
- 2.0 mL of concentrated nitric acid
- 1.0 mL of concentrated hydrochloric acid
- 50 µL of 2008Cal-1 stock standard from Inorganic Ventures
- 50 µL of 2008Cal-2 stock standard from Inorganic Ventures
- 400 uL of Internal Standard Working Solution
- Dilute to 100 mL mark with deionized water

7.23 Calibration Standard 2: For final concentrations and premixed standard concentrations, see Table 2. Into a 100 mL volumetric flask, add the following:

- Approximately 10 mL of deionized water.
- 2.0 mL of concentrated nitric acid
- 1.0 mL of concentrated hydrochloric acid
- 100 µL of 2008Cal-1 stock standard from Inorganic Ventures
- 100 µL of 2008Cal-2 stock standard from Inorganic Ventures
- 200 uL of Internal Standard Working Solution
- Dilute to 100 mL mark with deionized water

7.24 Calibration Standard 3: For final concentrations and premixed standard concentrations, see Table 2. Into a 100 mL volumetric flask, add the following:

- Approximately 10 mL of deionized water
- 2.0 mL of concentrated nitric acid
- 1.0 mL of concentrated hydrochloric acid
- 500 µL of 2008Cal-1 stock standard from Inorganic Ventures
- 500 µL of 2008Cal-2 stock standard from Inorganic Ventures
- 200 uL of Internal Standard Working Solution
- Dilute to 100 mL mark with deionized water

7.25 Continuing Calibration Verification Standard/Laboratory Fortified Blank: Same as ICV. See below.

7.26 NET-MSICV-1 stock standard from Inorganic Ventures: See Table 2 for content information.

7.27 NET-MSICV-2 stock standard from Inorganic Ventures: See Table 2 for content information.

7.28 Instrument Calibration Standard 1 stock standard from Spex: See Table 2 for content information.

7.29 Initial Calibration Verification Standard (ICV): For premixed standard and final concentrations see Table 2. Into a 250 mL volumetric flask, add the following:

- Approximately 10 mL of deionized water
- 5.0 mL of concentrated nitric acid
- 2.5 mL of concentrated hydrochloric acid
- 625 uL of NET-MSICV-1 stock standard from Inorganic Ventures
- 625 uL of NET-MSICV-2 stock standard from Inorganic Ventures
- 1000 uL of Internal Standard Working Solution
- Dilute to 250 mL mark with deionized water

NOTE: While both the calibration and ICV stock standards are purchased from the same vender (Inorganic Ventures), they are certified from that vender as being 2 separate sources. Additionally, the LFB stock standard does come from a second vender (Spex).

7.30 Laboratory Fortified Blank (LFB). Into a 250 mL volumetric flask, add the following:

- Approximately 10 mL of deionzed water
- 5.0 mL of concentrated nitric acid
- 2.5 mL of concentrated hydrochloric acid
- 625 uL of Instrument Calibration Standard 1 stock standard from Spex.
- 1000 uL of Internal Standard Working Solution
- Dilute to 250 mL mark with deionzed water

7.31 Reporting Limit Verification (RLV) Standard:

7.31.1 RLV Stock Working Solution. Into a 50 mL volumetric flask, add the following:

- Approximately 10 mL of deionzed water
- 1.0 mL of concentrated nitric acid
- 250 uL of NET-MSICV-1
- 250 uL of NET-MSICV-2
- Dilute to 50 mL mark with deionized water

7.31.2 Prepare RLV standards using the chart below.

	Conc. HNO_3	Conc. HCl	ICP-MS IS	RLV Stock	Final Volume
1.0 ug/L RLV	5 mL	2.5 mL	1000 uL	2.5 mL	250 mL
2.0 ug/L RLV	2 mL	1 mL	400 uL	2 mL	100 mL
4.0 ug/L RLV	2 mL	1 mL	400 uL	4 mL	100 mL
0.1 ug/L RLV	1 mL	0.5 mL	200 uL	100 uL	50 mL
0.2 ug/L RLV	1 mL	0.5 mL	200 uL	50 uL	50 mL

7.32 Rinse Blank Solution: The Rinse Blank Solution is used to clean out the sample lines and spray chamber between samples/standards. Into a 1 gallon plastic jug, add the following:

- Approximately ½ gallon of deionized water
- 80 mL of concentrated nitric acid
- 40 mL of concentrated hydrochloric acid
- Dilute to 1 gallon mark with deionized water

7.33 Calibration Blank: The Calibration Blank is used when calibrating the ICP-MS and is used as the Continuing Calibration Blank during the analytical run. The acid concentration in the Calibration Blank must match the acid concentration in the standards and samples. Into a 1 L volumetric flask, add the following:

- Approximately 100 mL of deionized water
- 20 mL of concentrated nitric acid
- 10 mL of concentrated hydrochloric acid
- Dilute to 1 L mark with deionized water
- Immediately transfer to a clean, plastic container for storage.
- This 2% HNO_3 / 1% HCl Dilution Solution will also be used when performing any required sample dilutions.

7.34 Preparation Blank: This blank is carried through the digestion procedure and contains the same volumes of reagents as the sample solutions.

7.35 Standard Shelf Life:

1 Year	10,000 and 1,000 μg/L Stock Solutions
1 Year	Premixed Standard Solutions
1 Year	Tuning Solution Stock (pre-mixed standard)
1 Month	Tuning Solution
1 Month	Internal Standard Stock Solution
1 Month	Hg Standard Stock Solution
1 Month	Hg ICV Stock Solution
7 Day	Calibration Standards
7 Day	Continuing Calibration Verification
7 Day	Initial Calibration Verification
7 Day	Reporting Limit Verification
7 Day	6020 ICS A and 6060 ICS AB Solutions

Note: Hg may be added to these standards for use in Potable analysis.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 When pre-preserved sample containers have been used for sample collection, it is the responsibility of the analyst to verify adequacy of preservation at the time the actual analysis is initiated.

8.2 All aqueous metals samples (except Cr VI) must be acidified to a pH of <2 with nitric acid upon collection. When nitric acid preserved containers are shipped to the client, use 2.5 mL of 1 part nitric to 2.5 parts water. Nonaqueous metals are refrigerated at <6°C, but not frozen.

8.3 Holding time is 180 days from collection.

9.0 Quality Control

9.1 Calibration Curve: A daily calibration curve consisting of a calibration blank and at least 3 multi-element standards, is constructed by plotting corrected extracted ion intensities against mg/L standard. The line that is generated must not be forced through the origin. The correlation coefficient must be 0.995 or greater using all calibration standards. Please refer to the QA Manual regarding protocols for dropping points of the calibration curve. If during the analytical run a CCV fails and corrective action is unsuccessful, the curve must be re-prepared/reanalyzed.

9.2 Initial Calibration Verification Standard (ICV) / Continuing Calibration Verification Standard (CCV): Analyze the ICV immediately following a calibration curve to verify the curve. Analyze the CCV after every 10th sample and at the end of the analytical sequence. The percent recovery acceptance criteria is ± 10% of the true value. If the ICV/CCV fails, it may be repeated one time. If the ICV/CCV still fails, re-evaluate the calibration curve to verify that all criteria have been met and verify the acceptability of the source used for preparing the ICV/CCV. If this does not solve the problem, reprepare/reanalyze the

calibration curve. All samples must be bracketed by passing CCVs. Samples not bracketed by passing CCVs must be reanalyzed.

9.3 Reagent Blank (RB) / Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB): Analyze the RB/ICB immediately following a calibration curve to verify the curve. Analyze the CCB after every 10th sample and at the end of the analytical sequence.

The following limits are monitored:

- If a value is greater than the Method Reporting Limit (MRL), all samples between that CCB and the previous passing CCB must be re-analyzed for that failing parameter.
- If a value is greater than 0.1 times the MRL, all samples between that CCB and the previous passing CCB must be:
  - Re-analyzed for that failing parameter; or
  - Reported as-is with an appropriate data qualification flag; or
  - Reported with an elevated MRL with an appropriate data qualification flag
- Values greater than 3 times the IDL but less than 0.1 times the MRL are monitored but do not require re-analysis or a data qualification flag.
- When analyzing samples that get reported down to the MDL, if a value is greater than the MDL but less than the MRL, all samples with hits above the MDL will be reported as-is with an appropriate data qualification flag.
- For all OVAP samples, contamination must be less than the Method Reporting Limit (MRL).

9.4 Preparation Blank (PB)/Method Blank (BLK): Analyze a minimum of one method blank (BLK) with each prep batch of 20 or fewer samples. This method blank is carried through the same procedures as a sample would go through.

The following limits are monitored:

- If a value is greater than the Method Reporting Limit (MRL), all samples in that batch must be re-digested and re-analyzed for that failing parameter. If a sample cannot be re-digested and re-analyzed, the data will be reported with an appropriate data qualification flag.
- If a value is greater than 0.1 times the MRL, all samples in that batch must be:
  - Re-digested and re-analyzed for that failing parameter; or
  - Reported as-is with an appropriate data qualification flag; or
  - Reported with an elevated MRL with an appropriate data qualification flag
- Values greater than 3 times the IDL but less than 0.1 times the MRL are monitored but do not require re-digestion and re-analysis or a data qualification flag.
- When analyzing samples that get reported down to the MDL, if a value is greater than the MDL but less than the MRL, all samples with hits above the MDL will be reported as-is with an appropriate data qualification flag.
- For all OVAP samples, contamination must be less than the Method Reporting Limit (MRL).

9.5 Laboratory Control Standard (LCS) / Blank Spike (BS): Analyze one mid- to high-level laboratory control standard (LCS) per every batch of 20 or fewer samples. The LCS is carried through the same procedure as a sample would go through. The current acceptance limits are located in the QA Manual. If the LCS is outside the acceptance limits for a particular parameter, it may be repeated one time. If the LCS is still outside of the acceptance limits, all samples prepared with the LCS in the batch must be re-prepped/reanalyzed for that parameter with the following exception:

- High Bias LCS recovery. In the event that a LCS recovery fails high for a specific parameter, associated samples in that batch are not required to be re-digested and re-analyzed if there was no detection for that parameter in those samples.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD): The MS/MSD pair are two sample aliquots spiked at known concentration that must be analyzed per every batch of 20 or fewer samples. These spikes must be carried through the same procedures, as a sample would go through. The current acceptance limits are located in the QA Manual. If the MS/MSD recoveries are not within the required acceptance limits, the MS/MSD results are reported with an appropriate data qualification flag.

- The MS/MSD are not used for batch control.

9.7 Reporting Limit Verification Standards (RLVs): The RLVs are standards that have concentrations at or below the established method reporting limits (MRLs) that are run after the instrument calibration. The acceptance criterion for this standard is ± 30% of the true value. If this criterion does not pass, the samples in the run must be repeated unless the following provisions are followed:

- If the RLV recovery is high, and the samples are non-detect for that specific analyte, then the data may be reported with flags.
- If the samples being analyzed have client required MRLs or permit limits that are greater than our standard MRLs, then the MRL may be elevated to the higher value of a another passing RLV standard, or to the level of the lowest point in the calibration curve.

9.8 Linear Range Analysis (LRA): The LRA is run annually or whenever is major change for instrumentation/standardization takes place. The linear range is established by analyzing multiple standards to determine the maximum concentration that each analyte is linear. There needs to be at least one standard for each order of magnitude above the calibration curve. The LRA recoveries must be within 90%-100%. Samples with results greater than 90% of the LRA must be diluted and re-analyzed.

- Table 9 lists the current Linear Range Limits, which are subject to change based on the LRA study.

9.9 Internal Standards (IS): The Internal Standards are elements that are similar to the elements that are being analyzed. Generally an internal standard should be no more than 50 amu removed from the analyte. The Internal Standards are added to all samples and QC Samples at a volume of 200 µL of IS to 50 ml sample/standard (or equivalent ratios such as 40 uL to 10 mL; 400 ug/L to 100 mL; 1000 ug/L to 250mL). For samples, the absolute response of any one internal standard must not deviate more than 30-120 % of the original response in the calibration blank. Table 3 shows the Internal Standard Concentrations.

9.9.1 The intensities of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below 30 percent of the intensity of that internal standard in the initial calibration blank, a significant matrix

effect must be suspected. Under these conditions, the detection limit has degraded and the correction ability of the internal standardization technique becomes questionable. The following procedure is followed: First, make sure the instrument has not just drifted by observing the internal standard intensities in the nearest clean matrix (initial calibration blank (ICB) or continuing calibration blank (CCB)). If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples. If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted twofold (1+1) or fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities rise above the 30 percent limit. Reported results must be corrected for all dilutions and with an appropriate data qualification flag.

9.9.2 While the criteria for Internal Standard recoveries for quality control standards (ICB, ICV, ICSA, ICSAB, RLVs, CCB, CCV, BLK, and BS) is not stated in Method 6020A, this laboratory has established that the internal standard must not deviate more than 60-125% of the original response in the calibration blank. If these requirements are not met, the solutions must be re-analyzed (or fresh solutions re-made and then re-analyzed). If these requirements are still not met, the analysis must be terminated, the problem corrected (to include such items as general instrument maintenance, cleaning, and conditioning), the instrument recalibrated and any affected samples reanalyzed.

9.10 <u>ICSA / ICSAB solutions:</u> The Interference Check Samples (ICS) are used to verify corrections for elemental and polyatomic isobaric interferences. The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of other analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A.

9.10.1 While specific ICSA/ICSAB criteria is not stated in Method 6020A, we follow the guidelines established in this SOP.

9.10.2 It should be noted that there are several interferents contained in the ICSA solution that are not part of our calibration or quantification report.

9.10.3 Analyze the ICSA and ICSAB solutions after calibration and every 12 hours of analysis time.

9.10.4 The analytical results of any quantified interfering analyte in the ICS Solution A (ICSA) must fall within +/-30% of the true value of that analyte (Al and Mo). Non-spiked analytes must be monitored to verify the absence of positive or negative effects from the interferent analytes contained in the ICSA solution. The absolute value of the results of the non-spiked analytes must be less than the Method Reporting Limit (MRL).

9.10.5 The analytical results of any quantified interfering analyte the ICS Solution AB (ICSAB) must fall within +/-30 of the true value of that analyte (Al and Mo). The analytical results of all other non-interfering spiked analytes in the ICSAB solution must fall within +/-20% of the true values of those analytes (As, Cd, Co, Cu Mn, Ni, Ag, and Zn).

9.10.6 If these requirements are not met, the ICSA/ICASB solutions must be re-analyzed (or fresh solutions re-made and then re-analyzed). If these requirements are still not met, the analysis must be terminated, the problem corrected (to include such

items as general instrument maintenance, cleaning, and conditioning as well as re-evaluation of correction equations), the instrument recalibrated and any affected samples reanalyzed.

9.11 Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, an analysis of a fivefold (1+4) dilution must agree within +/- 10% of the original determination. If not, an interference effect must be suspected and the data will be reported with an appropriate data qualification flag. One dilution test must be performed for every 20 samples or less of each matrix in a batch. The Post Dilution Test will be made as follows:

- Into a plastic disposable autosampler tube add 2 mL of prepared sample.
- Dilute to the 10 mL mark using the 2% HNO_3 / 1% HCl Dilution Solution.
- Add 40 uL of Internal Standard.
- Mix sample well.

9.12 Post digestion spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, must be recovered to within 75 to 125 % of the known value or within the laboratory derived acceptance criteria. If the spike is not recovered within the specified limits, the data will be reported with an appropriate data qualification flag. The use of a standard-addition procedure may also be used. One post digestion spike addition must be performed for every 20 samples or less of each matrix in a batch. Spiking information will be specified in ELEMENT so that recoveries can be calculated using the LIMS. Spike concentrations may be adjusted based upon the concentrations of metals present in the sample. Our standard Post digestion spike will be prepared as follows:

- Into a plastic disposable autosampler tube, added 10 mL of prepared sample or diluted sample if appropriate.
- Add 50 uL of Instrument Calibration Standard 1 from Spex
- Add 40 uL of Internal Standard.
- Mix sample well.

If the spike is not recovered within the specified limits the sample must be diluted and reanalyzed to compensate for the matrix effect.

10.0 Procedure

10.1 **Instrument Calibration and Sample Analysis**: Initiate the plasma and allow a warm-up for at least 10 minutes. The tuning procedures may be carried out during warm-up.

10.2 **Tuning Procedure:** Optimize the following parameters using the Tuning Solution.

Set RF power to desired level 1200 watts (1000-1100 watts for clean waters and 1200 watts for soil and sediments digests)

- Open “Performing X-Y Adjustment.wrk “workspace. Check and Adjust x-y positioning
- Optimize the nebulizer argon flow: Open “Optimizing Nebulizer Gas Flow.wrk” work space. Click on the tab “Auto Optomize.” Select “Nebulizer Gas Flow” under “Parameter Description. “Get Analyte List” Select “In 114.904”. Parameter Range Start Value 0.94, End Value 1.24, Set step value to 0.02 Optimization Criteria must be Maximium Intensities. Click on Optimize. The optimization will take a few

minutes. When finished set step value back to 0.005 and save the default.dac file and print graphic ion profile.

- Optimize the static lens voltage, Click on “Lens Voltage” under Parameter Description Analyte: In 114.904, Set parameter Range Start and Stop value. Step value must be 0.25 Optimization Criteria must be Maximium Intensities. Click on Optimize. When finished save default.dac file and print graphic ion profile

10.3 Perform the autolens calibration using the Tuning Solution and:

- Open TestAutolens.wrk workspace (Close Instrument panel) On the Optimization page select the “AutoLens” tab. Clear the old calibration
- Click on Get Analytes, Set the Start and End value, Step value should be 0.25
- Click on Calibrate (the procedure takes about 6 minutes)
- Save the default.dac file, print report, and graphic ion profiles

10.4 Check Mass Calibration and peak resolution (peak width)using these steps:

- Open “TestAtune.wrk” workspace. Click on tune mass spec
- Check that the resolution for all elements in the tuning file are (measured peak width) less than 0.65 amu (measured at 10% peak height) If the peak widths are greater than 0.65 amu. The resolution must also be verified to be less than 0.9 amu full width at 10 percent peak height.
- Peak width needs to be <0.9 amu at 10% peak height (See tuning mass spec)
- Measured Mass needs to be within 0.05 amu of the true mass (See tune mass spec)
- Increase the resolution DAC value for that element and run “tune mass spec” again.
- Check the mass calibration, if the measured mass is not greater than 0.05 amu from the true mass save the default.tune file. If the measured mass is greater than 0.05 amu click on “tune mass spec” again. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value.
- Print the Tuning report and the ion profile graphics ..

10.5 Open the Detector Cross Calib workspace (TestAcrosscalib.wrk)and aspirate a 200 mg/L solution containing all elements to be quantitated plus the internal standard elements and follow these steps:

- Select the tab (Dual Detector Calibration) Clear the old calibration
- Click on Get Analytes, Lens Voltage start value –3, end value 17 and step value 0.5.
- Click on calibrate
- Run the detector cross calibration routine
- Save the Optimization file(default.dac)
- Print out the Optimization file if needed.

NOTE: Do this step only on an as needed basis when a new detector is installed or the detector voltage changes or when the linear range check are out of control

10.6 Perform daily performance test (TestAdailyperformance.wrk): Aspirate the tuning solution, Adjust neb flow through the "Optimization manual adjust tab" so that Ce to CeO (oxides) and Ba to Ba++ (doubly charged) are equal to or below 0.030

- Click on analyze sample
- The RSD on 5 reading for Be, Mg, Rh and Pb must be $\leq$ 5%

10.7 **Calibration Standards Analysis**:

Open the workspace and prepare calibration standards and follow these steps:

- Make any desired changes to the method and save method.
- Load the calibration blank and the calibration standards into the autosampler positions specified in the autosampler page of the analytical method.
- Edit the sample page for batch analysis to update with new sample information.
- Load the applicable method for the sample batch. Note: If automatic QC checking is used the method must be the same for all samples.
- The Calibration Action for the first sample for which concentration results are desired must be "analyze blank, standards, and sample".
- The Calibration Action" for all other samples is usually "Analyze Sample", unless periodic recalibration is desired.
- Enter peristaltic pump speeds for all samples.
- Save Sample file.
- Load the sample into the autosampler positions specified in the Sample file.
- Select the sample to be analyzed by highlighting the row number with the mouse.
- Aspirate the rinse blank for 5 to 10 minutes before beginning the run to avoid carry-over and contamination.
- Select "Analyze Batch".

10.8 **Daily Analytical Sequence**

10.8.1 Calibration Blank: will zero the instrument

10.8.2 Calibration Curve: Blank plus three standards

10.8.3 Initial Calibration Verification Standard (ICV)

10.8.4 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB):

10.8.5 Continuing Calibration Verification Standard (CCV)/Laboratory Fortified Blank (LFB)

10.8.6 Reporting Limit Verification Standards (RLV)

10.8.7 ICSA and ICSAB solutions.

10.8.8 Preparation Blank (PB) / Method Blank (BLK)

10.8.9 Lab Control Standard (LCS) / Blank Spike (BS)

10.8.10 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

10.8.11 Dilution Test

10.8.12 Post digestion spike addition

10.8.13 CCB (after every 10th sample and at the end of the analytical sequence)

10.8.14 CCV (after every 10th sample and at the end of the analytical sequence)

11.0 **Calculations / Data Reduction**

11.0 All calculations for all analyses (standards and samples) are based on the average of three replicate instrument readings.

11.1 Standard Concentration Calculations. The concentration of each calibration standard is calculated from the concentration of the stock solution.

A generic formula is based upon the proportion, $C_1V_1 = C_2V_2$

Where: C_1 = Concentration 1 C_2 = Concentration 2

V_1 = Volume 1 V_2 = Volume 2

Example: $\frac{\text{1000 mg/L stock Standard x 1 mL}}{\text{100 mg/L}}$ = 10 mg/L

11.2 All calculations necessary to convert raw data (ion counts/second) are performed by the Elan software. The calculated quantities are selected by choosing the desired options in the Report Options screen. The default report option for the Elan 6020A Method is testA200 full QC report.rpo.

11.3 All calculations performed in the Elan software are based on the ratio of the analyte intensity (cps) to the internal standard intensity (cps). In all calculations where internal standard are used the ratio of analyte intensity to internal standard intensity is taken before any other calculation is performed.

11.4 Quality control results may be checked using the QC checking featured in the Elan software. All values entered in the default Elan software must be checked and edited before use.

11.5 Aqueous Sample Result in mg/L:

$$\text{Result (mg/L)} = \frac{\text{(Instrument Reading in mg/L) x (Dilution Factor of Sample) x (Final Volume)}}{\text{(Initial Volume)}}$$

11.6 Non Aqueous Sample Result in mg/Kg or µg/g:

$$\text{Result (mg/Kg or µg/g)} = \frac{\text{(Reading in mg/L) x (Final Volume in mL) x (Dilution Factor)}}{\text{(Weight of sample in g)}}$$

11.7 Spike Recovery of Matrix Spikes and Matrix Spike Duplicates:

$$\%\,\text{Recovery} = \frac{(S - U) \times 100)}{T}$$

Where:

S = Spiked result

U = Unspiked result

T = Spike True Concentration

ELEMENT will perform calculations when reporting results based on dry weight.

12.0 Method Performance

12.1 The supervisor has responsibility to ensure that an analyst who performs this procedure is properly trained in its use and has the required experience. Performance is monitored through internal QC and outside performance evaluation samples. Please refer to the QA Manual for additional information concerning Precision and Accuracy.

12.2 Demonstration of Capabilities - Prior to the analysis of samples, a Demonstration of Capabilities (DOC) as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.3 Method Detection Limit Study - A Method Detection Limit (MDL) study, as described in the QA Manual, must be performed initially, annually and any time a significant change is made to the analytical system.

12.4 Instrument Detection Limits Study - An IDL must be determined at least every three months and kept with the instrument logbook.

13.0 Waste Management and 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).

13.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in the Environmental Health & Safety Manual for "Waste Management and Pollution Prevention."

13.2 The following waste streams are produced when this method is carried out:

13.2.1 Acid waste consisting of sample and rinse solution is neutralized and discharged to the sanitary sewer.

14.0 References / Cross-References

14.1 Methods for Chemical Analysis of Water and Wastes, USEPA, Environmental Monitoring and Support Laboratory EPA-600/4-79-020.

14.2 SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", 3rd Edition, Method 6020, September 1986.

14.3 Users Manual for Perkin Elmer Elan 6000.

14.4 Method 200.8 using the ELAN 6000 ICP-MS, Perkin Elmer, Revision 1.0. 9/6/95 Draft.

15.0 Method Modifications

None

16.0 Attachments

Table 1 Common Molecular Ion Interferences in ICP-MS
- Background Molecular Ions
- Matrix Molecular Ions

Table 2 Commercially Available Stock Solutions
Table 3 Internal Standard Concentration
Table 4 Calibration Standard Concentration
Table 5 Initial Calibration Verification Standard
Table 6 Continuing Calibration Verification Standard
Table 7 Reporting Limit Verification Standard
Table 8 Example Reporting Limits
Table 9 Example Linear Range Limit
Table 10 Isotopes Monitored and Equations Used
Table 11 Example LCS and MS/MSD Concentrations For Digested Samples
Table 12 Interference Check Sample Elements and Concentration

17.0 Revision History

- Revision dated 8/29/07
  - New SOP

18.0 Contingencies

If for any reason a part of this SOP cannot be followed, seek the guidance of the Department Supervisor or Quality Assurance Department. Document all deviations on a Corrective Action Report and submit to the QA Quality Assurance Department.

This is an OVAP approved SOP. All changes, other than formatting or spelling, made to this SOP must be approved by OVAP prior to implementation.

Table 1 Common Molecular Ion Interferences in ICP-MS:

Background Molecular Ions		
Molecular Ion	**Mass**	**Element Interference**
NH^+	15	
OH^+	17	
OH_2^+	18	
C_2^+	24	

CN^+	26	
CO^+	28	
N_2^+	28	
N^2H^+	29	
NO^+	30	
NOH^+	31	
O_2^+	32	
O_2H^+	33	
$^{36}ArH^+$	37	
$^{38}ArH^+$	39	
$^{40}ArH^+$	41	
CO_2^+	44	
CO_2H^+	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	
$ArOH^+$	57	
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar^+$	78	Se
$^{40}Ar_2^+$	80	Se

Matrix Molecular Ions		
Molecular Ion	**Mass**	**Element Interference**
Bromide		
$^{81}BrH^+$	82	Se
$^{79}BrO^+$	95	Mo
$^{81}BrO^+$	97	Mo
$^{81}BrOH^+$	98	Mo
$Ar^{81}Br^+$	121	Sb
Chloride		
$^{35}ClO^+$	51	V

$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	77	Se
$^{32}SO^+$	48	
$^{32}SOH^+$	49	
$^{34}SO^+$	50	V, Cr
$^{34}SOH^+$	51	V
SO_2^+, S_2^+	64	Zn
$Ar^{32}S^+$	72	
$Ar^{34}S^+$	74	
PO^+	47	
POH^+	48	
PO_2^+	63	Cu
ArP^+	71	
Group I, II Metals		
$ArNa^+$	63	Cu
ArK^+	79	
$ArCa^+$	80	
Matrix Oxides		
TiO	62-66	Ni, Cu, Zn
ZrO	106-112	Ag, Cd
MoO	108-1116	Cd

Table 2 Commercially Available Stock Solutions

Solution ID	Manufacturer	Contents
Tuning Solution 1	Spex	10 mg/L each of Ba.Be, Ce, Co, In, Li, Mg, Pb, Rh, Tl U, Y 2% HNO_3/ 5% HCl
6020ISS	Inorganic Ventures	10 mg/L each of Bi, Ho, In, 6Li, Rh, Sc, Tb, Y in 5 % HNO_3
Germanium	Alfa Aesar	10,000 mg/L Ge 5% HNO_3/trace HF
CGAUN1-1	Inorganic Ventures	1,000 mg/L Au 1.4% HNO_3
Instrument Calibration Standard 1	Spex	20 mg/L each of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, Th, U,

		V, Zn 5% HNO_3/ trace Tart
NET-MSICV-1	Inorganic Ventures	20 mg/L each of Al, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, Th, U, V, and Zn in 3.5 % HNO_3
NET-MSICV-2	Inorganic Ventures	20 mg/L each of Sb and Mo in 2 % HNO_3, trace F^-
2008CAL-1	Inorganic Ventures	20 mg/L each of Sb and Mo in 2 % HNO_3, trace F^-
2008CAL-2	Inorganic Ventures	20 mg/L each of Al, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, Th, U, V, and Zn in 3.5 % HNO_3
6020ICS-8A	Inorganic Ventures	18,000 mg/L Cl, 3,000 mg/L Ca, 2,500 mg/L Fe and Na, 2,000 mg/LC, 1,000 mg/L Al, Mg, P, K, S, 20 mg/L Mo, Ti 1% HNO_3

Table 3 Internal Standard Concentration

Internal Standard (Analyte)	*Working Solution Concentration (mg/L)	**Sample Concentration (mg/L)
Lithium6 Li	9.6	0.0384
Beryllium, Be 9		
Scandium, Sc 45	9.6	0.0384
Beryllium, Be 9		
Aluminum, Al 27		
Vanadium, V 51		
Chromium, Cr 52		
Manganese, Mn 55		

Cobalt, Co 59		
Nickel, Ni 60		
Nickel, Ni-1 60		
Copper, Cu 63		
Copper, Cu 65		
Germanium, Ge 72	72.29	0.289
Zinc, Zn 64		
Zinc, Zn 66		
Zinc, Zn 68		
Arsenic, As 75		
Arsenic, As-1 75		
Selenium, Se 78		
Selenium, Se 82		
Yttrium, Y 89(alternate Int. Std)	9.6	0.0384
Indium, In 115	9.6	0.0384
Molybdenum, Mo 98		
Silver, Ag 107		
Cadmium, Cd 111		
Cadmium, Cd 114		
Antimony, Sb 121		
Antimony, Sb 123		
Turbium, Tb 159	9.6	0.0384
Holmium, Ho (alternate Int. Std)	9.6	0.0384
Barium, Ba 135		
Barium, Ba 137		
Mercury, Hg 201		
Mercury, Hg 202		
Thallium, Tl 205		
Lead, Pb (206+207+208)		
Bismuth, Bi 209(alternate Int. Std)	9.6	0.0384
Gold, Au ***		

*Note that the concentrations of the Internal Standard Working Solution are based on a final volume of 41.5 mL.
**Concentration when 200 µL of Internal standard is diluted to 50 mL in samples and standards.
***Added to aide in rinsing the system of mercury.
NOTE: Yttrium may present in environmental samples. Sc has polyatomic ion interference. Indium has isobaric interference from Sn. Yttrium may form YO^+ (105 amu) or YOH^+ (106 amu). This may effect the cadmium elemental correction equation.

Table 4 Calibration Standard Concentration

Element	STD1 (µg/L)	STD2 (µg/L)	STD3 (µg/L)
Al	10	20	100
Sb	10	20	100
As	10	20	100
Ba	10	20	100
Be	10	20	100
Cd	10	20	100
Cr	10	20	100
Co	10	20	100
Cu	10	20	100
Pb	10	20	100
Mn	10	20	100
Ni	10	20	100
Ag	10	20	100
Se	10	20	100
Tl	10	20	100
Zn	10	20	100

Table 5 Initial Calibration Verification Standard

Element	Concentration (µg/L)
Al	50
Sb	50
As	50
Ba	50
Be	50
Cd	50
Cr	50

Co	50
Cu	50
Pb	50
Mn	50
Ni	50
Ag	50
Se	50
Tl	50
Zn	50

Table 6 Continuing Calibration Verification Standard

Element	Concentration (µg/L)
Al	50
Sb	50
As	50
Ba	50
Be	50
Cd	50
Cr	50
Co	50
Cu	50
Pb	50
Mn	50
Ni	50
Ag	50
Se	50
Tl	50
Zn	50

Table 7 Reporting Limit Verification Standard

Element	RLV 0.1	RLV 0.2	RLV 1.0	RLV 2.0	RLV 4.0
	Concentration (µg/L)	Concentration (µg/L)	Concentration (µg/L)	Concentration (µg/L)	Concentration (µg/L)
Al	---	---	1.0	2.0	4.0
Sb	0.1	0.2	1.0	2.0	4.0
As	---	---	1.0	2.0	4.0
Ba	0.1	0.2	1.0	2.0	4.0
Be	0.1	0.2	1.0	2.0	4.0

Cd	0.1	0.2	1.0	2.0	4.0
Cr	---	0.2	1.0	2.0	4.0
Co	0.1	0.2	1.0	2.0	4.0
Cu	0.1	0.2	1.0	2.0	4.0
Pb	0.1	0.2	1.0	2.0	4.0
Mn	0.1	0.2	1.0	2.0	4.0
Ni	0.1	0.2	1.0	2.0	4.0
Ag	0.1	0.2	1.0	2.0	4.0
Se	---	0.2	1.0	2.0	4.0
Tl	0.1	0.2	1.0	2.0	4.0
Zn	---	---	1.0	2.0	4.0

Table 8 Example Reporting Limits

Element	Concentration (µg/L)
Al	50
Sb	1
As	5
Ba	5
Be	1
Cd	0.2
Cr	2
Co	5
Cu	5
Pb	1
Mn	10
Ni	5
Ag	0.5
Se	5
Tl	1
Zn	4

Table 9 Example Linear Range Limit

Element	Concentration (µg/L)

Al	1,800
Sb	1,800
As	1,800
Ba	1,800
Be	1,800
Cd	1,800
Cr	1,800
Co	1,800
Cu	1,800
Pb	1,800
Mn	1,800
Ni	1,800
Ag	100
Se	1,800
Tl	1,800
Zn	1,800

Table 10 Isotopes Monitored and Equations Used

Element	Isotopes Monitored	Equations Used
Al	27	
Sb	121,123	Sb 123 = Sb 123 - 0.127189*Te 125
As	75	As 75 = As 75 - 3.127*(ArCl 77-(0.815*Se82))

As-1	75	“As 75-1” = ”As 75-1” – 3.127*(Se 77-(0.3209*Se 78))
Ba	135,137	
Be	9	
B	10	
Cd	111	Cd 111 = Cd 111 - 1.073*(MoO 108 – (0.712*Pb 106))
Cd	114	Cd 114 = Cd114 – 0.026826 * Sn 118
Ca	44	
Cr	52,53	
Co	59	
Cu	63,65	
Fe	54	Fe54=Fe54 - 0.028226*Cr52
Pb	206,207,208	Pb 208 = Pb 208 + 1*Pb206 + 1*Pb207
Mg	24	
Mn	55	
Hg	202	
Mo	95,97,98	Mo 98 = Mo 98 - 0.110588 * Ru 101
Ni	60	Ni 60 = Ni 60 – 0.0044 * Ca 43
Ni-1	60	
K	39	
Se	78	Se 78 = Se 78 – 0.030461 * Kr 83
Se	82	Se 82 = Se 82 - 1.008696 * Kr 83
Ag	107,109	
Na	23	
Tl	203,205	
Th	232	
Sn	118	
Ti	48	
U	238	
V	51	V 51 = V 51 – 3.127*(ClO 53 - (0.113 * Cr 52))
Zn	64,66,68	Zn 64 = Zn 64 – 0.035313 * Ni 60
Li	6	
Sc	45	
Y	89	
Rh	103	
In	115	In 115 = In 115 – 0.014032 * Sn 118
Tb	159	
Bi	209	
Ge	72	

Table 11 Example LCS and MS/MSD Concentrations For Digested Samples

Element	Aqueous Conc. (µg/L)	Element	Aqueous Conc. (µg/L)
Al	50	Cu	50
Sb	50	Pb	50
As	50	Mn	50
Ba	50	Ni	50
Be	50	Ag	50
Cd	50	Se	50
Cr	50	Tl	50
Co	50	Zn	50

Table 12 Interference Check Sample Elements and Concentration

	Solution A ICSA mg/L	**Solution AB ICSAB**
Al	10.0	10.0
Ca	30.0	30.0
Fe	25.0	25.0
Mg	10.0	10.0
Na	25.0	25.0
P	10.0	10.0
K	10.0	10.0
S	10.0	10.0
C	20.0	20.0
Cl	180.0	180.0
Mo	0.20	0.20
Ti	0.20	0.20
As	0.0	0.0200
Cd	0.0	0.0200
Cr	0.0	0.0200
Co	0.0	0.0200
Cu	0.0	0.0200
Mn	0.0	0.0200
Ni	0.0	0.0200
Ag	0.0	0.0200
Zn	0.0	0.0200
Se	0.0	0.0200
V	0.0	0.0200

CHLORINATED HERBICIDES BY GC/ECD: PREPARATION AND ANALYSIS

(Methods: EPA 515.1, EPA 615, and EPA 8151A)

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1.0 Scope and Application

This SOP gives the procedures for the determination of chlorinated herbicides by gas chromatography/electron capture detection (GC/ECD). The routine sample matrices associated with this procedure are waters and soils. Other, non-routine matrices may be incorporated as outlined in Section 16.0.

A complete target analyte list, the reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

2.1 Sample Preparation

2.1.1 Water Samples – A known volume of aqueous sample, nominally 1000mL, is transferred to a Teflon separatory funnel. The sample is hydrolyzed with base to convert the herbicides present to their salt form. The hydrolyzed sample is extracted with methylene chloride to remove the non-phenoxy acid herbicide material. The sample is acidified and extracted with diethyl ether. The extract is dried, filtered, concentrated, esterified with diazomethane, dissolved in MTBE, and analyzed by GC/ECD.

2.1.2 Soil Samples – A known weight of a sample, approximately 30g wet weight, is acidified with hydrochloric acid (HCl) and combined with acidified sodium sulfate to form a free flowing, sandy mixture. Diethyl ether is added to the dried sample, and the sample is extracted using an ultrasonic disrupter for 9 minutes. The extract is transferred to a separatory funnel containing water that has been adjusted to pH$\geq$12. The sample is allowed to hydrolyze for one hour to convert the acid and ester forms of the herbicides to their salt forms. The solvent is discarded, and the aqueous phase, which contains the herbicides in their salt form, is acidified and extracted with diethyl ether. The extract is dried, concentrated, esterified with diazomethane, dissolved in MTBE, and analyzed by GC/ECD.

2.2 Sample Analysis

The extracted methyl derivatives are analyzed by a GC equipped with dual capillary columns (different phases) connected to dual electron capture (EC) detectors, allowing simultaneous detection and confirmation of the target compounds. Quantitation is performed using the external standard calibration technique.

2.3 This SOP is based on the following methods: EPA 515.1, EPA 615, and EPA 8151A.

3.0 Definitions

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Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

Note: The glassware used for herbicides must not be used to extract or concentrate dioxins and furans. Several of the herbicides are precursors to the formation of dioxins or are associated with the presence of dioxins in the environment

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid, methanol, methylene chloride, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.1.5 The base hydrolysis step removes interferences from the sample extract. Dinoseb, a phenolic herbicide, is very reactive and will have poor recoveries when subjected to the base hydrolysis step.

4.1.6 Injection port maintenance is very important for the consistent detection of the reactive herbicides such as dinoseb.

4.1.7 The acid forms of the analytes are strong organic acids which react readily with alkaline substances and can be lost during sample preparation. Glassware and glass wool must be acid-rinsed with 1N hydrochloric acid or acidified methanol and the sodium sulfate must be acidified with sulfuric acid prior to use to avoid analyte losses due to adsorption.

4.1.8 Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. Alkaline hydrolysis and subsequent extraction of the basic sample removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

4.1.9 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the ECD. These compounds generally appear in the chromatogram as large peaks. Common flexible plastics contain varying amounts of phthalates, that are easily extracted or leached during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted

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surfaces are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive purification of reagents and glassware may be required to eliminate background phthalate contamination.

4.1.10 It is important that samples and working standards be contained in the same solvent. The solvent for working standards must be the same as the final solvent used in sample preparation. If this is not the case, chromatographic comparability of standards to sample may be affected.

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. The method provides a Florisil cleanup procedure to aid in the elimination of interferences that may be encountered. Refer to Attachment 9 for instructions.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

4.2.3 Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction. Emulsions will occur most readily during the "base shake" to remove the non-target compounds. The extract may be filtered or stirred to remove the emulsion or may be "salted out" by the addition of sodium chloride.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, 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 to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

5.1 Specific Safety Concerns or Requirements

5.1.1 Sample Preparation

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The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard. Exposure to these chemicals should be minimized.

The use of separatory funnels to extract aqueous samples with solvents creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This step is considered a high-risk activity, and a face shield must be worn over safety glasses or goggles when performed.

Ultrasonic disrupters can produce high intensity noise and must be used in an area with adequate noise protection.

Diethyl ether is a flammable solvent that can cause drowsiness. The extraction analyst using diethyl ether must not work alone in an isolated area of the lab. A solvent such as diethyl ether can cause a burning sensation when it contacts the skin. The rapid evaporation of the solvent causes a rapid heat loss in the skin, which is similar to frost bite. If this occurs, rinse the exposed skin in cold water to reduce the solvent evaporation.

Due to the flammable nature of diethyl ether, if a mechanical device is used for sample extraction it should be equipped with an explosion-proof motor and placed in a hood to avoid possible damage and injury due to an explosion.

The lab should keep only the minimum supply of diethyl ether. Diethyl ether will form explosive peroxides if stored in the lab for long periods of time. Opened containers of diethyl ether must be checked monthly for peroxides using peroxide test strips using the following steps:

- *Remove 1 test strip and immediately close the test strip tube.*
- *Dip the test strip into the solution to be tested for 1 second, such that the reaction zone is completely wetted.*
- *Move the test strip slightly back and forth for 3-30 seconds until the solvent has evaporated from the reaction zone, then*
  - *Dip into distilled water for 1 second, shake off excess water, or*
  - *Breathe on test strip 4 times each for 3-5 seconds*
- *After 15 seconds, compare the reaction zone with the color scale.*
- *If the color scale indicates the presence of peroxides, then dispose of the contents of the container as directed in the TestAmerica Savannah Addendum to the EHSM.*

Hexane is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, lightheadedness, headache, dizziness, and blurred vision.

Hydrochloric acid is extremely hazardous as an oxidizer, a corrosive, a poison, and is reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Methanol is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, confusion, headache, dizziness, and drowsiness.

Sodium hydroxide is a severe corrosive. Contact with the skin can cause irritation or severe burns and scarring. Contact with the eyes can cause irritation, burns, permanent vision impairment or even blindness.

Sulfuric acid is a strong oxidizer and is a corrosive. It will react violently when combined with organic compounds, possibly producing fire. Inhalation can cause irritation of the nose, throat, mucus membranes, and upper respiratory tract. Contact with the eyes can cause blurred vision, redness, pain, and even blindness.

Diazomethane is a toxic carcinogen which can explode under certain conditions. In order to minimize safety hazards the diazomethane generation apparatus used in the esterification procedure produces micromolar amounts of diazomethane. Even with this precaution, the following procedures should be followed: Use only a well ventilated hood (do not breath vapors) with a safety screen. Use mechanical pipetting aides. Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips. **EXPLOSION** may result if the following occur: heating above 90°C, grinding surfaces, ground glass joints, sleeve bearings, glass stirrers, or storage with alkali metals.

5.1.2 Sample Analysis

Hexane is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, lightheadedness, headache, dizziness, and blurred vision.

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

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. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

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Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Hexane	Flammable Irritant	500ppm TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Hydrochloric Acid	Corrosive Poison	5ppm Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methanol	Flammable Poison Irritant	200ppm TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methyl Tert-Butyl Ether	Flammable Irritant Poison	50ppm TWA	Inhalation of vapor can irritate respiratory tract. Breathing high concentrations in air can cause lightheadedness, dizziness, weakness, nausea, and headache. Ingestion may cause vomiting with symptoms similar to inhalation. Can cause irritation to skin and eyes with possible damage to the eye tissue.
Ethyl Ether, Diethyl Ether	Flammable Irritant Peroxide Former	400ppm TWA	General anesthesia by inhalation can occur. Continued exposure may lead to respiratory failure or death. Early symptoms include irritation of nose and throat, vomiting, and irregular respiration, followed by dizziness, drowsiness, and unconsciousness. May cause irritation, redness and pain to the eyes. Irritating to the skin and mucous membranes by drying effect. Can cause dermatitis on prolonged exposure. May be absorbed through skin. **May form explosive peroxides on long standing or after exposure to air or light. This material must be disposed of with six months.**

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Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Sodium Hydroxide	Corrosive	2mg/m^3 Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1mg/m^3 TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
[1]Exposure limit refers to the OSHA regulatory exposure limit.			
Note: Always add acid to water to prevent violent reactions.			
TWA – the time-weighted average exposure limit: the maximum average concentration of a chemical in air for a normal 8-hour working day and 40-hour week Ceiling – the concentration that should not be exceeded at any time STEL – short-term exposure limit: the maximum average concentration to which workers can be exposed for a short period (usually 15 minutes)			

6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

6.1.1 Sample Preparation

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Ultrasonic disrupter – Tekmar Model or equivalent with horn-type titanium-tipped sonication probe. The sonicator should be capable of operating in the pulse mode at full power.

Sonabox – the sonicator must be placed in the sonabox to reduce noise. The sonabox must be placed under a fume hood.

Diazomethane generator

NOTE: If the herbicide blank is contaminated, clean the generator tubing and vessels with methylene chloride, methanol, and diethyl ether, in that order, and purge the

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apparatus with nitrogen to dry. Replace the Teflon tubing and vessels if the solvent cleaning does not improve the blank.

Kuderna-Danish apparatus – consists of the K-D body, three-ball Snyder column, and a graduated concentration tube with springs or clips to hold the concentration tube to the K-D body. Verify the concentration tube in accordance with SOP SA-AN-30: *Pipette and Volumetric Container Calibration Verification.*

Water bath – compatible with the K-D apparatuses, located under an operating fume hood

6.1.2 Sample Analysis

Gas Chromatograph (GC) – temperature programmable, equipped with dual electron capture (EC) detectors and a compatible autosampler. The laboratory currently uses an Agilent 6890 GC with dual micro-cell electron capture detectors and an Agilent 7683 autosampler.

The following column pairs are recommended. Other columns/phases may be used if the calibration and QC criteria are met and adequate separation of the target compounds is achieved.

J&W DB-XLB 30m x 0.32mm ID x 0.5um film
J&W DB-35MS 30m x 0.32mm ID x 0.5um film

6.2 Analytical Data System / Software / Hardware

Chemstation software is used on a Windows-based PC to schedule and acquire data. Target (UNIX and/or Windows) software is used on a Windows-based PC to store, reduce/evaluate, and output the data to the laboratory's LIMS system (i.e., TALS). Target software has the capability of processing stored GC data by recognizing a GC peak within any given retention time window and comparing the retention time of the sample to the retention times of the standards analyzed under the same conditions. The software also allows calculation integration of the peak responses, response factors, construction of a linear regression calibration curve, calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the response factors.

6.3 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Disposable Transfer Pipettes – various sizes

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Gas-Tight Syringes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

6.1.3 Sample Preparation

Separatory Funnels – 1L and 2L, Teflon with Teflon stopcocks. Glass funnels may also be used.

Large Funnels

Pyrex Glass Wool – rinse with acidified methanol prior to use

Stainless Steel Spatulas

Pre-Cleaned 500mL Extraction Bottles – Discard after use.

1L Pre-Cleaned Containers – This is the same container used to collect the sample and can be used to collect the aqueous phase during the solvent wash. Discard after use.

Filter paper – grade 414, 18.5cm diameter

Extract Vials – 12mL vials with Teflon-lined caps

Peroxide Test Strips

Detergent – FL-70, used for washing non-disposable labware.

pH paper – provides a quick and easy way to approximate the pH of a sample to determine if a sample has been properly preserved or if the pH of a sample is in the proper range for a preparation step.

Residual (free) chlorine powder pillows – HACH; Catalogue #2105569

Medicine cups – 30mL, disposable

Stainless steel measuring cup – 1/3 cup

6.1.4 Sample Analysis

Autosampler Vials, Septa, and Caps – compatible with the autosampler

6.2 <u>Sample Collection Containers</u>
All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are:

Waters
1L Amber Glass – purchased with Certificate of Analysis attesting to purity.

Soils

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16oz. Soil Jar – purchased with Certificate of Analysis attesting to purity.

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

Unless listed elsewhere in this SOP, the expiration dates given below apply.

7.1.1 The expiration date for unopened standards and reagents is the manufacturer's expiration date.

7.1.2 The expiration date for opened stock reagents is the manufacturer's expiration date or 5 years from the date opened, whichever is sooner.

7.1.3 The expiration date for opened stock standards is the manufacturer's expiration date or 6 months from the date opened, whichever is sooner.

7.1.4 The expiration date for prepared reagents is 6 months from the date prepared or the expiration date of the parent reagent, whichever is sooner.

7.1.5 The expiration date for prepared standards is 3 months from the date prepared or the expiration date of the parent standard, whichever is sooner.

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures.*

Hydrochloric acid, methanol, and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

7.2.1 Purchased Reagents

7.2.1.1 Sample Preparation

7.2.1.1.1 Blank Matrix – Teflon chips, glass beads, or equivalent. Used for the preparation of soil QC samples.

7.2.1.1.2 Laboratory Reagent Water – ASTM Type II

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7.2.1.1.3 Sodium Sulfate – powdered and granular, anhydrous
Storage: Consignment room; Store in a tightly closed container in a cool, dry, ventilated area. Separate from incompatibles.

7.2.1.1.4 Methanol – residue grade or better
Storage: Consignment room; Store in a flammable storage cabinet, away from incompatibles (acids, bases). Isolate from heat and ignition sources.

7.2.1.1.5 Diethyl Ether – residue grade or better. Check periodically for formation of peroxides as described in Section 5.1.1.
Storage: Consignment room; Store in a flammable storage cabinet, away from incompatibles (acids, bases). Isolate from heat and ignition sources.

7.2.1.1.6 Sodium Hydroxide (NaOH) – reagent grade
Storage: Consignment room; Store in a cool, dry, ventilated area, away from incompatibles (acids, organics).

7.2.1.1.7 Sulfuric Acid (H_2SO_4) – concentrated reagent grade
Storage: Consignment room; Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.

7.2.1.1.8 Hydrochloric Acid (HCl) – concentrated, reagent grade
Storage: Consignment room; Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.

7.2.1.1.9 Potassium Hydroxide (KOH) – reagent grade
Storage: Consignment room; Store in a cool, dry, ventilated area, away from incompatibles (acids, organics).

7.2.1.1.10 Diazald (N-methyl-N-nitroso-p-toluenesulfonamide) – reagent grade
Storage: 0-6°C; SM/EX refrigerator; Store in a tightly closed container, away from heat, sparks or open flames.

7.2.1.1.11 Carbitol – reagent grade or better
Storage: 0-6°C; SM/EX refrigerator

7.2.1.1.12 Silica Gel – reagent grade
Storage: Soil extractions room

7.2.1.1.13 MTBE – residue grade or better
Storage: Consignment room; Store in a flammable storage cabinet, away from incompatibles (acids, bases). Isolate from heat and ignition sources.

7.2.1.1.14 Sodium Chloride – granular, anhydrous
Storage: Store in a tightly closed container in a cool, dry, ventilated area. Separate from incompatibles.

7.2.1.2 Sample Analysis

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7.2.1.2.1 MTBE – residue grade or better
Storage: Consignment room; Store in a flammable storage cabinet, away from incompatibles (acids, bases). Isolate from heat and ignition sources.

7.2.2 Prepared Reagents

7.2.2.1 Sample Preparation

7.2.2.1.1 Baked Sodium Sulfate – purify the Sodium Sulfate by heating at 400°C for four hours in a shallow tray.
Storage: Soils lab
Expiration: 1 year from preparation date

7.2.2.1.2 Acidified Sodium Sulfate – Transfer purified sodium sulfate to a suitable glass container until the container is about ¾ full. Working under a hood, add enough diethyl ether to wet the sodium sulfate. Add 10mL of concentrated sulfuric acid for each kilogram of sodium sulfate and stir to mix the acid into the solvent and sodium sulfate. Add more diethyl ether to keep the sodium sulfate wet while stirring the sodium sulfate. The acid must be thoroughly mixed into the sodium sulfate and diethyl ether. Pour off the excess solvent and allow the diethyl ether to evaporate under a hood for 24 hours. Store in a glass container. Check the pH of the acidified sodium sulfate by mixing 1g and 5mL of water in a small container. The pH of the solution should be less than 4.
Storage: Glass container, at 130°C
Expiration: 3 months

7.2.2.1.3 Sodium Hydroxide Solution (10N) – Dissolve 400g of NaOH pellets into about 500mL reagent water contained in a 2-L beaker on a magnetic stirrer. Add the NaOH in small portions, with constant stirring, to minimize the time it takes to dissolve the pellets. A good deal of heat will be generated as the NaOH dissolves. After all 400g have been added, carefully dilute to 1000mL with reagent water. Mix the solution thoroughly and transfer to a storage container. Do not store sodium hydroxide solution in volumetric glassware or in containers with ground glass joints.
Storage: Liquid-Liquid extraction Room
Expiration: 1 year from preparation date

7.2.2.1.4 Potassium Hydroxide Solution (37%) – Weigh 37g of KOH into a 100-mL volumetric flask and dilute to volume with reagent water.
Storage: Liquid-Liquid extraction Room
Expiration: 1 year from preparation date

7.2.2.1.5 Acidified Methanol (approximately 0.12N) – Carefully add 10mL of concentrated HCl to the 4L methanol container.
Storage: Liquid-Liquid extraction Room
Expiration: 3 month from preparation date

7.2.2.1.6 Baked Blank Matrix – purify the blank matrix by heating at 400°C for four hours in a shallow tray.
Storage: Soils extraction lab
Expiration: 1 year from preparation date

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7.2.2.1.7 Baked Sodium Chloride – purify the Sodium Chloride by heating at 400°C for four hours in a shallow tray.
Storage: Soils extraction
Expiration: 1 year from preparation date

7.3 Standards

Standards must be prepared and documented in accordance with SOP SA-AN-41: *Reagent and Standard Materials Procedures*. Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

Note: EPA 515.1 samples analyzed for the Wisconsin Department of Natural Resources (WI DNR) must be analyzed against standards prepared in accordance with the WI DNR Project Requirements Summary (PRS).

Note: The values present in the LIMS Reagent Program for the analytical standards do not directly match the COA from the vendors. The LIMS values are the values present on the vendor COA and are adjusted by the correction factor equation given below. This correction factor is needed since the standard is expressed as mass of ester per volume.

$$CF = \frac{MW\,acid}{MW\,ester}$$

7.3.1 Purchased Standards

7.3.1.1 Sample Preparation

7.3.1.1.1 DCAA (1000ug/mL) – Surrogate, prepared in methanol, purchased from Accustandard
Storage: 0-6° C; EX/SM Refrigerator

7.3.1.1.2 Chlorinated Herbicides Mixture (varying concentrations) – prepared in methanol, purchased from Ultra
Storage: 0-6° C; EX/SM Refrigerator

7.3.1.1.3 Herbicide Additions Mix (200ug/mL) – prepared in methanol, purchased from Restek
Storage: 0-6° C; EX/SM Refrigerator

7.3.1.2 Sample Analysis

Note: Herbicide analysis standards are purchased as methyl esters; therefore, the concentration of the standard must be corrected to the free acid concentration. This will eliminate the need to correct the final concentration of the sample. The correction factors are given in Attachment 5.

7.3.1.2.1 Herbicide Methyl Ester Mix (MCPA/MCPP at 20000ug/mL; Dalapon at 1000ug/mL; 2,4-D, 2,4-DB, 2,4,5-T, 2,4,5-TP, Dicamba, Dichlorprop, and Dinoseb at 100ug/mL) – prepared in Hexane, purchased from NSI.

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Storage: 0-6°C; SG Refrigerator

7.3.1.2.2 Pentachloroanisol (100ug/mL) – prepared in methanol, purchased from Accustandard
Storage: 0-6°C; SG Refrigerator

7.3.1.2.3 DCAA Methyl Ester (100ug/mL) – prepared in MTBE, purchased from Ultra
Storage: 0-6°C; SG Refrigerator

7.3.1.2.4 Picloram Methyl Ester (100ug/mL) – prepared in Methanol, purchased from Accustandard
Storage: 0-6°C; SG Refrigerator

7.3.1.2.5 DCPA (1000ug/mL) – prepared in Restek, purchased from Methanol
Storage: 0-6°C; SG Refrigerator

7.3.1.2.6 Herbicide Additions Mix (200ug/mL) – prepared in Methanol, purchased from Restek
Storage: 0-6°C; SG Refrigerator

7.3.1.2.7 Herbicide Methyl Ester Mix, Second Source (MCPA/MCPP at 10000ug/mL; Dalapon at 1000ug/mL; 2,4-D, 2,4-DB, 2,4,5-T, 2,4,5-TP, Dicamba, Dichlorprop, and Dinoseb at 100ug/mL) – prepared in methanol, purchased from Ultra
Storage: 0-6°C; SG Refrigerator

7.3.1.2.8 Pentachloroanisol, Second Source (100ug/mL) – prepared in methanol, purchased from Chemservice
Storage: 0-6°C; SG Refrigerator

7.3.1.2.9 Picloram Methyl Ester, Second Source (1000ug/mL) – prepared in methanol, purchased from Restek
Storage: 0-6°C; SG Refrigerator

7.3.1.2.10 DCPA (100ug/mL), Second Source – prepared in methanol, purchased from Ultra
Storage: 0-6°C; SG Refrigerator

7.3.2 Prepared Standards

7.3.2.1 Sample Preparation

7.3.2.1.1 Herbicide Surrogate Spiking Solution

Herbicide Surrogate Spiking Solution

Stock Standard	Parent Concentration (ug/mL)	Aliquot (mL)	Final Volume (mL)	Final Concentration (ug/mL)
DCAA	1000	1.0	500	2.0

Solvent: Methanol
Storage: 0-6°C; EX/SM Refrigerator

7.3.2.1.2 Herbicide Spiking Solution

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Herbicide Spiking Solution

Stock Standard	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Chlorinated Herbicides Mixture	200/20,000	1	100	2.0/200

Solvent: Methanol
Storage: 0-6° C; EX/SM Refrigerator

Herbicide Spiking Solution

Stock Standard	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Herbicide Additions Mix	200	1	100	2.0

Solvent: Methanol
Storage: 0-6° C; EX/SM Refrigerator

7.3.2.2 Sample Analysis

7.3.2.2.1 Intermediate Calibration Stock Standard

Intermediate Calibration Stock Standard

Stock Standard	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Herbicide Methyl Ester Mix	*	125	10	2.5, 25, 500
Pentachloroanisol	100	175		1.75
DCAA Methyl Ester	100	250		2.5
Picloram Methyl Ester	100	250		2.5
DCPA	1000	40		4.0

* MCPA/MCPP at 20000ug/mL; Dalapon at 1000ug/mL; 2,4-D, 2,4-DB, 2,4,5-T, 2,4,5-TP, Dicamba, Dichlorprop, and Dinoseb at 100ug/mL.

Solvent: MTBE
Storage: 0-6° C; EX/SM Refrigerator

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7.3.2.2.2 Calibration Standards

Cal Level	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Cal Level 1	See Section 7.3.2.2.1	100	10	0.025, 0.25, 5.0
Cal Level 2		200	10	0.050, 0.50, 10
Cal Level 3		400	10	0.10, 1.0, 20
Cal Level 4		3000	50	0.15, 1.5, 30
Cal Level 5		800	10	0.20, 2.0, 45
Cal Level 6		1000	10	0.25, 2.5, 50
Cal Level 7		2000	10	0.50, 5.0, 100

Solvent: MTBE
Storage: 0-6°C; EX/SM Refrigerator

7.3.2.2.3 Intermediate Calibration Stock Standard for Wisconsin DNR Samples

Stock Standard	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Chlorinated Herbicides Mixture	*	250	10	2.5, 25, 500

* MCPA/MCPP at 20000ug/mL; Dalapon at 1000ug/mL; 2,4-D, 2,4-DB, 2,4,5-T, 2,4,5-TP, 2,6-D, 2,4,6-T, Dicamba, Dichlorprop, Dinoseb, and picloram at 200ug/mL; Pentachloroanisole at 133ug/mL; DCPA at 320 ug/mL.

Solvent: MTBE
Storage: 0-6°C; EX/SM Refrigerator

7.3.2.2.4 Wisconsin DNR Calibration Standards

Cal Level	Parent Concentration (ug/mL)	Aliquot (uL)	Final Volume (mL)	Final Concentration (ug/mL)
Cal Level 1	See Section 7.3.2.2.3	100	10	0.025, 0.25, 5.0
Cal Level 2		200	10	0.050, 0.50, 10
Cal Level 3		400	10	0.10, 1.0, 20
Cal Level 4		3000	50	0.15, 1.5, 30
Cal Level 5		800	10	0.20, 2.0, 45
Cal Level 6		1000	10	0.25, 2.5, 50
Cal Level 7		2000	10	0.50, 5.0, 100

Solvent: MTBE
Storage: 0-6°C; EX/SM Refrigerator

Note: Wisconsin calibration standards are to be made using the free acids listed above. Once the working levels of the calibration have been made they are to be

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esterified prior to analysis.

8.0 Sample Collection, Preservation, Shipment, and Storage

8.1 Aqueous Samples

Aqueous samples for EPA 615 and EPA 8151A are routinely collected in 1L amber glass containers. Aqueous samples for EPA 515.1 are routinely collected in 1L amber glass containers containing sodium thiosulfate de-chlorination agent. The dechlorination agent should be sufficient to remove residual chlorine from the sample.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples for EPA 615 and EPA 8151A must be prepared within 7 days of collection. Samples for EPA 515.1 must be prepared within 14 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis. Extracts for EPA 615 and EPA 8151A must be analyzed within 40 of extraction. Extracts for EPA 515.1 must be analyzed within 28 days of extraction.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives and/or de-chlorination agents.

8.1.1 Preservation Checks – Residual Chlorine

These checks can be performed upon receipt or prior to preparation.

8.1.1.1 Mix the sample by inverting and transfer 10mL to a small medicine cup.

8.1.1.3 Add a residual chlorine powder pillow to the sample in the cup and note the presence of a pink color, which indicates the presence of residual chlorine. If the sample tests positive for residual chlorine, initiate an NCM noting that residual chlorine was present. Add sodium sulfite in small aliquots to the sample container and retest 10mL portions of the sample until the sample is negative for residual chlorine.

8.2 Soil Samples

Soil samples are routinely collected in 16oz soil jars.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation. Samples must be prepared within 14 days of collection. Extracts must be stored at 4°C (less than 6°C but not frozen) until the time of analysis and analyzed within 40 days of extraction.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

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An extraction batch consists of up to 20 environmental samples and the associated QC items extracted together within a 24 hour period.

The laboratory's default QC items required for each extraction batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS) – to be performed on a minimum of 10% of samples in a batch (for EPA 515.1 and EPA 615) or 20% of samples in a batch (for EPA 8151A), and a matrix spike duplicate (MSD).

This frequency equates to the following:

- For a batch of 10 or fewer samples, the minimum QC items are a method blank, an LCS, 1 matrix spike, and 1 matrix spike duplicate.
- For a batch of 11-20 samples, the minimum QC items are a method blank, an LCS, 1 matrix spike (from sample 1-10), another matrix spike (from sample 11-20, for EPA 515.1 or EPA 615 only), and a matrix spike duplicate.

The routine container supplied for this method is a 1L container for waters and a 16oz container for soils. 1L is the default extraction volume for waters, and 30g is the default extraction amount for soils. Reduced sample initial volumes and amounts may be necessary to achieve the required batch matrix spike frequency; however, the minimum extraction volume to be used for the matrix spike samples is 500mL for waters and 15g for soils. Note: Final volumes and spike amounts must be adjusted to compensate for these reduced initial volumes.

If there is insufficient sample volume to perform the required matrix spike(s), the LCS must be prepared in duplicate (i.e., LCS/LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 2L for waters and 60g for soils.

Note: If an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required.

Note: The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water samples, an LCS at the RL must also be included in the required batch QC.

Batch QC must meet the criteria given in Attachment 3 of this SOP.

9.2 Instrument QC

9.2.1 Initial Calibration (ICAL)

The instrument must be calibrated in accordance with SOP SA-QA-16: *Evaluation of Calibration Curves*. This SOP provides requirements for establishing the calibration curve and gives the applicable formulas.

Instrument calibration is performed by analyzing a series of known standards. The calibration curve for EPA 8151A must consist of a minimum of 5 standards. The calibration curve for EPA 615 must consist of a minimum of 3 standards. The calibration curve for EPA 515.1 must consist of a minimum of 3 (recommend 5) standards. The

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lowest level calibration standard must be at or below the reporting limit, and the remaining standards will define the working range of the analytical system.

The initial calibration standard concentrations currently in use in the laboratory are provided in Section 7.3.2.2. Refer to Section 7.3.2.2 for the standard preparation instructions. Other standard concentrations may be used provided they support the reporting limit and are fully documented in accordance with SOP SA-AN-41.

9.2.2.1 ICAL Criteria

For EPA 515.1 and EPA 8151A, the relative standard deviation of the calibration standards must be <20% for the initial calibration curve to be acceptable. For EPA 615, the relative standard deviation of the calibration standards must be <10% for the initial calibration curve to be acceptable.

The preferred method of quantitation is the average response or calibration factor. If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve.

The regression coefficient (r^2) of the regression curve must be greater than 0.990 for the initial calibration curve to be acceptable.

Note: A minimum of 5 points is required for a linear curve. A minimum of 6 points is required for a quadratic curve. Higher order curves are not permitted. Some programs and agencies (e.g., SC DHEC) do not allow the use of quadratic curves. Refer to the Project Requirement Summary and/or Project Plan to determine if this curve type is prohibited.

Grand Mean Exception – EPA 8151A
SW-846 allows the use of the "grand mean exception" as described below. This exception should only be applied to initial calibration curves in extraordinary circumstances because of the difficulty of maintaining and providing documentation on an on-going basis.

Grand Mean Exception (GME): If one or more analytes exceed the %RSD criteria, the calibration curve is acceptable if the average of the %RSDs for all of the analytes in the ICAL (i.e., the grand mean) is less than or equal to the ICAL %RSD criteria.

SW-846 does not place a cap on an individual analyte's %RSD as long as the average is within criteria; however, the laboratory has adopted the requirement that no individual analyte can exceed 3X the ICAL criteria. Therefore, the calibration curve is acceptable if the average of the %RSDs is less than or equal 20% with no individual analyte exceeding 60%.

Note: Some programs and agencies do not allow the use of the grand mean exception. Refer to the Project Requirement Summary and/or Project Plan to determine if GME is not allowed.

9.2.2 Second Source Initial Calibration Verification (ICV)

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The calibration curve must be verified initially – prior to any sample analyses – in accordance with SOP SA-QA-16 with a standard obtained from a second source.

The ICV for EPA 515.1 must be within 20% to be acceptable.

The average %D for the ICV for EPA 615 and EPA 8151A must be within 15% with no single analyte greater than 45% to be acceptable.

The initial calibration verification standard concentration currently in use in the laboratory is equivalent to level 4 of the ICAL. Refer to Section 7.3.2.2 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

Note: This standard must be analyzed at least quarterly for EPA 515.1. If the instrument does not require calibration after 3 months, the ICV must be analyzed.

9.2.3 Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

The instrument must be shown to be free from contamination by the analysis of calibration blanks. Initial calibration blanks are analyzed at the beginning of each clock. Continuing calibration blanks are analyzed after each CCV.

Initial and continuing calibration blanks must be <1/2RL to be acceptable.

9.2.4 Continuing Calibration Verification

9.2.4.1 EPA 515.1

The initial calibration curve must be verified initially, every 24 hours or 20 samples, and at the end of the sequence. The concentration of the CCV must be varied with each clock.

The CCV for EPA 515.1 must be within 20% to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to levels 4 and 3 of the ICAL. Refer to Section 7.3.2.2 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.4.2 EPA 615

The initial calibration curve must be verified initially and every 24 hours (each working shift) or 20 samples, with a mid-level standard.

The CCV for EPA 615 must be within 10% to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to level 4 and 3 of the ICAL. Refer to Section 7.3.2.2 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

9.2.4.3 EPA 8151A

The initial calibration curve must be verified initially, every 12 hours or 20 samples, and at the end of the sequence with a mid-level standard.

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The CCV for EPA 8151A must be within 15% to be acceptable.

The continuing calibration verification standard concentration currently in use in the laboratory is equivalent to level 4 and 3 of the ICAL. Refer to Section 7.3.2.2 for the standard preparation instructions. Another standard concentration may be used provided it is mid-level and fully documented in accordance with SOP SA-AN-41.

Grand Mean Exception – EPA 8151A
SW-846 allows the use of the "grand mean exception" as described below.

Grand Mean Exception (GME): If one or more analytes exceed the %D criteria, the calibration curve is acceptable if the average of the %Ds for all of the analytes in the CCV (i.e., the grand mean) is less than or equal to the CCV %D criteria.

SW-846 does not place a cap on an individual analyte's %D as long as the average is within criteria; however, the laboratory has adopted the requirement that no individual analyte can exceed 3X the CCV criteria. Therefore, the CCV is acceptable if the average of the %Ds is less than or equal 15% with no individual analyte exceeding 45%.

Note: Some programs and agencies do not allow the use of the grand mean exception. Refer to the Project Requirement Summary and/or Project Plan to determine if GME is not allowed.

9.2.5 Surrogate

This procedure uses surrogates to evaluate the extraction process. DCAA is the surrogate.

Prior to preparation, this surrogate is added to all samples and QC items. The concentration of the surrogate is the same in all field samples and QC samples. A concentration of 2.0ug/L is used.

The percent recovery of the surrogate in all field samples and QC samples must be within the limits listed in the Method Limit Groups (MLGs) in LIMS. If the percent recovery is outside of this range, the analysis of the sample must be repeated. Repeated failure of the surrogate percent recovery may indicate re-extraction is necessary.

9.2.6 Laboratory Performance Check Sample (LPC)

EPA 515.1 requires the analysis of a Laboratory Performance Check (LPC) Sample daily. The LPC includes checks for instrument sensitivity (using dinoseb), chromatographic performance (using 4-Nitrophenol), and column performance (using 3,5-Dichlorobenzoic acid and 4-Nitrophenol).

The evaluation criteria for the LPC are included in Attachment 6.

If the criteria in Attachment 6 are not met, the instrument system will need to be re-evaluated. This can include routine maintenance and/or replacement of analytical columns.

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9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05, *Preventive and Corrective Action Procedures* and the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Aqueous Sample Preparation

10.1.1 Inspect the samples. Determine if the samples have multiple layers such as a sediment or an oil layer. Samples with large amounts of sediments or particulates may clog the stopcock on the separatory funnel. Consult with the Department Manager or Technical Manager if the sample matrix is unusual or is difficult to categorize. An NCM must be initiated to denote any unusual sample preparation steps required prior to the extraction.

Mark the level of the sample on the outside of the container. This marking will be used to determine the original sample volume actually used in the extraction process as follows: after the sample has been added to the separatory funnel, fill the empty sample container with water to the mark. Pour the water into a graduated cylinder, and determine the volume. Record the volume log to the nearest 5mL.

10.1.2 Add 1000mL of reagent water to each of two separatory funnels to serve as the method blank and laboratory control sample (LCS). Add 1.0mL of surrogate to each sample, MS, and MSD (directly to the original sample container) as well as to the method blank and LCS. Add 1.0mL of spiking solution to all LCS, MS, and MSD.

10.1.3 Thoroughly mix the sample by inverting the container several times and pour the entire contents of the sample into a properly labeled 2L Teflon separatory funnel.

Add approximately 50mL methylene chloride to the sample container. Swirl the solvent around the inside of the container to thoroughly rinse the sample bottle and add this rinse to the separatory funnel.

Using a stainless steel measuring cup, add 1/3 cup of granular NaCl to each sample, MB, LCS, MS, and MSD.

10.1.4 Adjust the pH of the sample to >12 with 10N NaOH. Check the pH with narrow range pH paper. Allow the samples to stand for at least one hour with intermittent shaking or shake on the automatic shaker for one hour.

Note: This step is necessary to convert the acid and ester forms of the herbicides to the water-soluble salts. After the hydrolysis step, the non-target compounds are extracted out of the sample with methylene chloride. The rest of the extraction steps may be performed with manual or automatic shaking.

10.1.5 Add 100mL of methylene chloride to each separatory funnel.

10.1.6 Shake each separatory funnel for ten minutes with periodic venting to release any excess pressure. If an automatic shaker is used, shake the samples for ten minutes. Allow ten minutes for complete separation between the lower solvent and upper water phases.

Note: The separatory funnel should be vented under a hood to remove the solvent fumes from the lab.

10.1.7 Drain the lower layer (methylene chloride) into a designated waste container.

Note: Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction. Emulsions will occur most readily during the "base shake" to remove the non-target compounds. The extract may be filtered or stirred to remove the emulsion.

10.1.8 Adjust the pH of each of the samples and QC items to <2 with 10mL sulfuric acid. Add the acid slowly and gently swirl the separatory funnels to ensure that the acid and base have reacted. Acid/base neutralization reactions can be violent if mixed too quickly. Check the pH of the samples and QC items to ensure that the pH < 2.

10.1.9 Add 250mL of diethyl ether to each sample and QC item.

-If performing a "manual shake", shake the funnels for one minute, venting frequently to release any pressure.
-If using the automatic shaker, shake the samples continuously for thirty minutes, releasing the pressure periodically.

10.1.10 After the extraction, allow the layers to separate for at least ten minutes. Collect the water layer (lower layer) in a large beaker or flask and discard this layer.

10.1.11 Collect the extract (upper layer) into a 500-mL pre-cleaned extraction bottle containing 30g acidified sodium sulfate. Allow the extract and sodium sulfate to remain in contact at least two hours but preferably overnight.

10.1.12 Concentrate the extract to a final volume of approximately 10mL using the K-D apparatus in a water bath set at a temperature of approximately 70°C.

The extract may be left in the 10mL graduated concentrator tube or transferred to a labeled storage vial. The extract is now ready for the diazomethane esterification.

10.2 Soil Sample Preparation

10.2.1 Remove samples to be extracted from the storage refrigerator and allow the samples to reach room temperature while the extraction glassware is being prepared.

Check the "tune" of the sonicator using the procedure in SOP SA-EX-40: *Ultrasonic Extraction.*

10.2.2 Collect the appropriate glassware and rinse with acidified methanol and diethyl ether prior

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to use.

10.2.3 Open the sample container and inspect the sample. Note any unusual characteristics such as the presence of rocks, sticks, leaves, or other materials. Soil samples must be homogenized prior to preparation in accordance with SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples.*

Note: If it is difficult to homogenize the sample or if the sample matrix is difficult to characterize, contact the Department Manager before proceeding with the extraction. A careful inspection of the sample at this point can save time and effort later on in the analysis. Any unusual sample preparation steps required prior to the extraction must be noted on a Nonconformance Report.

10.2.4 Weigh 30.0-31.0g of the homogenized sample into a pre-cleaned, labeled 500mL extraction bottle. Record the weight to the nearest 0.1g for all samples in this batch.

Weigh 30.0-31.0g of blank matrix into two separate beakers to serve as the method blank and laboratory control sample (LCS). Weigh additional 30.0-31.0g portions of the samples selected as the MS and MSD.

10.2.5 Working under a hood, acidify each sample and QC item with 0.1 to 0.2mL of concentrated hydrochloric acid. Add the acid to the sample slowly and carefully, stirring the sample with a stainless steel spatula, glass rod, or pipette. Continue to add acid until the pH <2 when read with narrow range pH paper.

10.2.6 Add sodium sulfate to each non-porous or wet sample (gummy or clay-type) and QC item. Stir with a glass rod or stainless steel spatula to form a sandy, free-flowing mixture. The sodium sulfate combines with the water in the sample to "dry" the sample (remove the water). More sodium sulfate may be required if the sample is very wet. Proceed to the next step as quickly as possible.

Add 1.0mL of the herbicide surrogate spiking solution to the method blank, LCS, MS, MSD, and each sample in the batch. Add 1.0mL of the herbicide spiking solution to the LCS, MS, and MSD. Transfer the extraction bottles to a hood near the sonicator.

10.2.7 Under a hood, add 250mL of diethyl ether to each sample and QC item. Stir the sample to break up any lumps that may have formed. Add more solvent until the solids are covered by about one inch.

10.2.8 Place the tip of the sonicator horn in the center of the beaker about ½ inch below the surface of the solvent but above the solid portion.

10.2.9 Sonicate for nine minutes with the output control knob set at 10, mode switch to pulse, and percent duty cycle set at 50%. If the sonication is properly performed, the solids and solvent will vigorously mix each time the sonicator pulses.

10.2.10 Add 500mL of reagent water to a 2L Teflon separatory funnel. Adjust the pH of the water to pH >=12 using 10N KOH. Transfer the entire extract to the separatory funnel, using several small aliquots of diethyl ether to rinse the bottle.

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Check the pH with narrow range pH paper. Allow the sample to stand for at least one hour with intermittent shaking or shake on the automatic shaker for one hour.

Check the pH again after the one hour time period. If the pH <12, adjust the pH to >= 12 and allow to stand or shake for an additional hour. The pH must remain at or above 12 during the hydrolysis step.

Note: This step is necessary to convert the acid and ester forms of the herbicides to the water-soluble salts. After the hydrolysis step, the non-target compounds are contained in the diethyl ether layer.

Discard the diethyl ether layer and retain the water layer for additional preparation steps. The rest of the extraction steps may be performed with manual or automatic shaking. The sample extraction/preparation steps from this point forward are the same as described in Sections 10.1.3 through 10.1.11.

10.3 Esterification with Diazomethane

10.3.1 After sample concentration has been performed, the sample will need to be esterified with diazomethane. Concentrate the extracts to approximately 1mL under a gentle stream of nitrogen using the N-Evap apparatus.

10.3.2 After all of the extracts have been concentrated, prepare the diazomethane generation device for the esterification. Inspect the lines to ensure that there are no leaks or broken connections.

10.3.3 Place the extracts on the support. Replace all of the needles, and place the needles into the first extracts to be esterified.

10.3.4 Add diethyl ether to the first container on the diazomethane generation device until the container is about ¾ full.

10.3.5 Add the following to the second container to esterify approximately 20 samples:

50mL diethyl ether
50mL 37% potassium hydroxide
50mL Carbitol
5g Diazald

Note: Smaller volumes and weights of reagents may be used if the ratios above are maintained.

Quickly attach the container to the diazomethane device and start the nitrogen flow. Recall that the needles should already be placed in the samples that are to be esterified first. The gas flow should be steady but not so high that the sample is bubbled out of the concentrator tube or that the sample is evaporated before the esterification can take place.

10.3.6 Allow the diazomethane to flow through the sample extracts until a persistent yellow color remains. This will usually take two to three minutes. The esterification process will take longer as the diazomethane is exhausted.

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Note: For dark extracts where the persistent yellow color cannot be distinguished, esterify the samples for 10 minutes.

10.3.7 After the persistent yellow color remains, remove the needle from the tube in that position and replace it with a new needle. Place the needle into the next sample to esterify. Repeat for all samples in the batch, replacing the needle for each new extract. If a yellow color cannot be formed in a clear extract, the diazomethane has most likely been exhausted. Pour the used reagents into a waste container (under a hood) and replenish the reagents in the second container. Add more diethyl ether to the first container if needed.

10.3.8 After all of extracts have been esterified, add a small amount (about 0.1g) of silica gel to each sample extract, cover the concentrator tubes with aluminum foil and allow the extracts to sit for 30 minutes. The silica gel will destroy any un-reacted diazomethane. Dilute to 10mL with MTBE and transfer the extract to a labeled storage vial. Store the extracts at 4°C until the time of analysis.

10.2 Analysis

10.3.1 Instrument Operating Conditions

The instrument conditions listed in this SOP are provided for guidance purposes. The actual conditions used by the laboratory may be slightly different from those listed here and must be documented in the instrument maintenance log, data system, and/or run log.

Instrument maintenance must be performed in accordance with Attachment 4 of this SOP.

The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

Two columns are connected to the injection port using a press-tight glass y-splitter and a guard column, a two-hole ferrule, or a glass tee to provide simultaneous detection and confirmation of the target analytes.

Example GC Parameters
Injector: 240°C
Detector: 300°C
Carrier Gas Flow: Helium at ~2mL/min (per column) (pressure at 20psi, constant)
Make-up Gas Flow: Nitrogen at ~60mL/min (per detector)

Temperature Program:

Initial Temp:	50°C
Initial Hold:	0.50 min
Program Rate 1:	12°C/min to 100°C
Program Rate 2	15°C/min to 200°C
Program Rate 3:	80°C/min to 300°C
Final Temp:	300°C (hold for 1.25 minutes)
Total Time:	15.73 minutes
Injected Volume:	1uL per column (single injection into guard column and "Y" splitter)

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10.3.1.1 Determination of Retention Time Windows

The procedure for the determination of retention time windows is given in SOP SA-QA-08: *Evaluation of Chromatographic Data.* Retention time windows (RTW), i.e., the length of time the instrument will scan for the analyte, must be established initially upon instrument set-up and verified quarterly.

Retention times (RT), i.e., the elution time of the analyte, are verified daily with the analysis of the ICAL or CCV. The retention time for the CCV must fall within the daily retention time window as defined in SOP SA-QA-08.

10.3.2 Initial and Continuing Calibration

Calibrate the instrument using the standards and criteria described given in Section 9.2.1. Once the calibration has been established and verified with an ICV in accordance with Section 9.2.2, sample analysis may proceed.

Verify the calibration curve with a continuing calibration verification using the standards and criteria described given in Section 9.2.4.

10.3.3 Sample Analysis

Remove the extracts from the refrigerator and allow them to come to room temperature.

The sample extract must be injected using the same injection volume used for the calibration standards. Samples that are known to be relatively clean should be analyzed first. Samples suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

The default procedure is to exclude QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the clock.

10.3.4 Example Analytical Sequence

An example analytical sequence is provided in Attachment 1.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data evaluation must be performed in accordance with SA-QA-08: *Evaluation of Chromatographic Data.* This SOP includes specific information regarding the evaluation of chromatographic data, including the requirements for performing manual integrations and the evaluation of retention times.

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review.*

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11.1.1 Target Analyte Identification

The judgment and experience of the analyst and his/her colleagues are important factors in the evaluation of chromatographic data. Inspect each chromatogram to ensure that the peaks are properly identified and that the correct areas have been associated with the corresponding standard peak RT in the data system tabulation.

The evaluation of chromatograms for target compounds must take into account the calibration of the analytical system (initial and continuing calibration response and retention times); the recovery and retention time shift of the surrogate compounds, whether the peak response falls within the working range of the calibration; and the integration of the peaks. The analyst must also take into account the results from the method blank and lab control sample before reporting quantitative data. SOP SA-QA-08: *Evaluation of Chromatographic Data* provides additional guidance for the evaluation of chromatographic data. This guidance is summarized in the following sections.

11.1.2 Manual Integrations

Manual integrations must be documented in accordance with SOP SA-QA-08. Data systems should be adjusted to minimize operator intervention. All chromatographic peaks must be evaluated for overall peak shape and "reasonableness" of integration. Under no circumstances should manual integrations be used to change reasonable data system integrations in order to meet calibration or QC criteria.

11.1.3 Dual Column Reporting

Refer to SOP SA-QA-08: *Evaluation of Chromatographic Data* for information on assessing and reporting data from dual columns.

11.1.4 Surrogate Evaluation

One surrogate, DCAA, is spiked into each sample and QC item prior to preparation. Given the complicated nature of GC-ECD chromatograms, assessing surrogate recovery is frequently complicated by co-eluting positive and negative interferences. Evaluate the surrogates in the same manner as the target compounds using the guidance above.

11.1.5 Dilutions

If the response for an analyte exceeds the working range of the system, a dilution is required. Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags must be used or qualification in a case narrative provided to the client.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 5 to provide lower reporting limits.

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11.1.5.1 Surrogate Dilution Threshold Factor

Surrogates may be diluted out if the concentration of target compounds is high or the presence of non-target compounds interferes with the quantification of the target compounds. Undetect surrogates in the sample when the dilution factor is 6 or greater. As such, recoveries must be reported as "0D", and control limits will not apply.

An NCM must be initiated to denote this situation.

11.1.5.2 Dilutions and MS/MSD Recoveries

Matrix spike recoveries are not reported for dilutions of 5 or greater. An NCM is generated for instances where the dilution prohibits evaluation of the MS/MSD recoveries. In instances where the unspiked sample concentration is more than four times the concentration of the target compound spiked into the MS and MSD, the results are qualified with "4" or other suitable flag.

An NCM must be initiated to denote this situation.

11.1.6 Chemical Relationships and Compounds of Concern

Dalapon - this compound elutes very early in the run and may be subject to interference from co-eluting compounds and from artifacts from the extraction process.

MCPA and MCPP - these compounds have very low response in comparison to the other herbicides.

Dinoseb - this compound can be lost in the extraction process (hydrolysis step) but also may be lost if the injection port is not frequently and properly maintained.

11.1.7 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify TALS Worksheet Notes or use the TALS Historical Data Tracker feature to determine if historical data is available for review.

11.1.8 Drinking Water Compliance Evaluation

Public water suppliers (PWS) are governed by EPA-specified Maximum Contaminant Levels (MCL) above which indicates noncompliance. The MCLs associated with this procedure are given in Attachment 7. Notify the PM immediately via a Nonconformance Memo if any sample contains a detection above these levels.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculations associated with initial and continuing calibrations and are given in SOP SA-QA-16. Applicable calculations include determination for: calibration factor, standard

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deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$Final\,Concentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

Where:

$CONC_{Sample}$= Concentration of the sample
F = Final volume/weight
I = Initial volume/weight
dw = % Solids decimal equivalent
D = Dilution factor

Note: This calculation assumes all applicable unit correction factors are applied.

Note: All dry weight corrections are performed automatically in LIMS.

Note: Methyl ester herbicide standards must be corrected to the free acid concentration. This is performed by comparing the molecular weight of the methyl ester to that of the acid to determine a correction factor. Attachment 5 gives the molecular weights of the acids and esters. It also lists the correction factors and illustrates how to perform the acid-ester correction.

12.0 Method Performance

12.1 Reporting Limit Verification (RLV)

At a minimum, RLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, RLVs must also be performed quarterly thereafter. For all other analytes and methods, RLVs must also be performed annually thereafter. Exceptions may be made for project-specific non-routine analytes.

12.2 Method Detection Limit (MDL) Study

The 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. 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 current MDLs associated with this procedure are given in the Method Limit Group (MLG) in TALS.

At a minimum, MDL Studies must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits.*

Note: MDL Studies are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

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12.3 Method Detection Limit Verification (MDLV)

At a minimum, MDLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, MDLVs must also be performed quarterly thereafter. For all other analytes and methods, MDLVs must also be performed annually thereafter.

Note: MDLVs are not required for non-routine analytes provided results are not reported below the RL (i.e., MDL equals RL in TALS).

12.4 QC Limit Generation, Control Charting, and Trend Analysis

EPA 515.1 and EPA 615
The control limits for the batch QC items (LCS, MS/MSD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data*.

EPA 8151A
The control limits for the batch QC items (LCS, MS/MSD) for this procedure are not specified by the reference method; therefore, the laboratory defaults to in-house and/or laboratory-derived limits for the evaluation of batch QC items.

Control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data*.

12.5 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06: *Training Procedures*.

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four

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consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.6 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Flammable wastes (hexane, methanol, diethyl ether, diazald) – Transfer to flammable waste containers. Transfer to hazardous waste section when the satellite container is 95% full.

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15.0 References / Cross-References

- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-AN-41: *Reagent and Standard Materials Procedures*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-08: *Evaluation of Chromatographic Data*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-16: *Evaluation of Calibration Curves*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual
- *Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846*; including Updates III and IV. U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, November, 1986.
  - Method 8000B: *Determinative Chromatographic Separations*, Revision 2; December 1996
  - Method 8151A: *Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization*, Revision 1; December 1996
- *Code of Federal Regulations, Title 40, Part 136*; U.S. Government Printing Office: Washington, DC, July 1, 1988.
  - Method 615: *the Determination of Chlorinated Herbicides in Municipal and Industrial Wastewater*
- *Code of Federal Regulations, Title 40, Part 141*; U.S. Government Printing Office: Washington, DC, July 1, 1988, and Part III, March 12, 2007.
- Method 515.1: *Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector*, Revision 4.0, U.S. EPA, Cincinnati, OH 45268

16.0 Method Modifications and Clarifications

16.1 Incorporation of Other Matrices

The EPA 515.1 reference method was written specifically for drinking water and source water samples; however, the laboratory may perform other types of water samples by this method.

This procedure may be modified to analyze other matrices (e.g., wipe, waste, and leachate samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project.

Wipe, waste, and leachate matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.), and soil QC limits to evaluate these types of samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for wastes and wipes.

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16.1.1 Waste Samples

Waste samples are extracted as follows:
Weigh 1.0-1.2g of the homogenized sample into a calibrate 12mL vial. Fill to vial to the mark with diethyl ether. Proceed to Section 10.1.3 and complete the preparation.

16.1.2 Wipe Samples

Wipe samples are prepared as follows:
Add diethyl ether to the sample until the volume comes up to the shoulder of the vial, leaving some headspace between the top of the solvent and the vial cap. Shake the vials for 1-2 minutes.

Set up a 2L separatory funnel for each sample and QC item. Add 500mL of reagent water to each funnel. Adjust the pH of the water in each funnel to >=12 with 10N sodium hydroxide.

Transfer the entire contents of the vial to the separatory funnel. Rinse the vial with several small aliquots of ethyl ether and add to the funnel.

Shake for one hour on the automatic shaker. Check the pH of the sample. If the pH >=12, continue on to Section 10.1.4 and complete the sample preparation. If the pH<12, add more 10N sodium hydroxide and shake for an additional 15 minutes. Continue until the pH is >=12. Proceed to Section 10.1.4 and complete the preparation.

Note: Since the same site cannot be used to collect another wipe sample, MS and MSD are not applicable to this preparation.

16.1.3 Leachate Samples

TCLP and SPLP samples are prepared as follows:
Transfer 10mL of the leachate to a separatory funnel and dilute to 500mL with reagent water. Proceed to Section 10.1.3 and complete the preparation.

16.2 Other Considerations

16.2.1 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each EPA 515.1 batch of drinking water samples. The EPA DW Manual does not specify criteria for the low-level LCS; therefore, the laboratory defaults to 50-150%.

16.2.2 EPA Method 515.1 requires a Quality Control Sample (QCS) obtained from a source external to the laboratory and different from the source of calibration standards to be analyzed quarterly. The laboratory uses the second source initial calibration verification (ICV) to meet this requirement.

16.2.3 The laboratory prepares water samples for EPA 515.1, EPA 615, and EPA 8151A in the same manner (i.e., as mandated in EPA 515.1). Both EPA 615 and EPA 815A and associated EPA Memoranda provide allowances to adjust sample preparation procedures in this fashion provided method-defined quality control criteria are met. Further

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information on this change is provided below:

Diethyl ether is used as the extraction solvent for soils in place of 1:1 acetone/methylene chloride. This step was modified to improve recovery of chlorinated herbicides. Recoveries of the herbicides using acetone/methylene chloride were found to be less than 10%. The initial extract of soils is not concentrated prior to hydrolysis. The entire extract is transferred to a separatory funnel containing water that has been adjusted to pH >=12 for hydrolysis.

The extraction procedure has been modified from the guidance provided in EPA 8151A. The table below summarizes the differences.

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Extraction Step	EPA 8151A	SOP
Extraction of non-targets from hydrolyzed (basic) sample (essentially a cleanup step)	3x60mL MeCl2. Shake each aliquot for 2 minutes.	1x100mL MeCl2. Shake for 10 minutes on automatic shaker.
Extraction of herbicides from acidified sample (post hydrolysis)	120mL ethyl ether, then 2x60mL ethyl ether Shake each aliquot for 2 minutes.	1x300mL ethyl ether. Shake for 30 minutes on automatic shaker.

The laboratory's procedures are adapted from Section 11.2 of EPA Method 515.1, Revision 4. These modifications minimize transfer of the sample between containers which minimizes the loss of target analytes due to absorption on the glassware.

All batch QC samples, MDL studies, DOCs, and PT samples have been performed utilizing the method modifications listed above. Acceptable recoveries/results have been obtained indicating these modifications do not have a negative impact on the performance of this method.

16.2.4 EPA 515.1 lists mercuric chloride as a preservative for EPA 515.1 but acknowledges extreme health hazards associated with this chemical. As such, the laboratory has not incorporated the use of this chemical.

16.2.5 Unless specifically required to do otherwise (i.e., WI DNR compliance samples), the laboratory's default procedure is to incorporate the use of purchased methyl ester calibration standards instead of the free acids forms. All method validation steps (e.g., MDLs, DOCs, PTs, etc.) have been performed in this manner, and adverse results have not been noted

16.2.6 The reference methods specify continuing calibration verifications to be performed either every 12 hours (EPA 8151A) or every 24 hours (EPA 515.1 and EPA 615). The laboratory requires a capping CCV to be performed every 20 field samples or 12 or 24 hours, whichever comes first.

16.2.7 The laboratory uses its in-house control limits to evaluate initial demonstrations of capability.

16.2.8 EPA 515.1 does not provide criteria for initial calibration curves (i.e., non-RSD evaluation). The laboratory has adopted a r^2 criteria of 0.990 which is consistent with EPA 8151A. EPA 615 and EPA 8151A do not require analysis of a 2nd source ICV. This standard has been adopted to meet NELAC requirements. A 20% D criteria has been imposed for these methods, which is equivalent to the CCV criteria in EPA 615.

16.2.9 EPA 515.1 specifies to add 250g of sodium chloride per sample during the extraction process. The laboratory uses 1/3 cup sodium chloride (equivalent to approximately 100g) as its default amount as previous tests have indicated excess sodium chloride can adversely affect recoveries. 100g is sufficient to change the polarity of the sample enough to allow the compounds of interest to be extracted into diethyl ether and to prevent emulsions from occurring.

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16.2.10 In an effort to meet some client- and/or state-specific requirements for batch precision, the laboratory's default batch QC items have been expanded from those outlined in the reference methods (i.e., to include MSD and/or LCSD).

16.2.11 EPA 515.1 Revision 4.1 was released by the EPA and then recalled due to QC requirements mandated for dinoseb that could not routinely be achieved by laboratories. As instructed by EPA, the method cited by the laboratory is the earlier version (i.e., EPA 515.1 Revision 4.0).

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Herbicide Molecular Weights and Correction Factors
Attachment 6: EPA 515.1 Laboratory Performance Check (LPC) Evaluation Criteria
Attachment 7: EPA-specified Maximum Contaminant Levels (MCL)
Attachment 8: Glassware Cleaning
Attachment 9: Florisil Clean-up Procedures

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Attachment 1:
SOP Summary

Sample Preparation Summary
Water Samples – A known volume of aqueous sample, nominally 1000mL, is transferred to a Teflon separatory funnel. The sample is hydrolyzed with base to convert the herbicides present to their salt form. The hydrolyzed sample is extracted with methylene chloride to remove the non-phenoxy acid herbicide material. The sample is acidified and extracted with diethyl ether. The extract is dried, filtered, concentrated, esterified with diazomethane, dissolved in MTBE, and analyzed by GC/ECD.

Soil Samples – A known weight of a sample, approximately 30g wet weight, is acidified with hydrochloric acid (HCl) and combined with acidified sodium sulfate to form a free flowing, sandy mixture. Diethyl ether is added to the dried sample, and the sample is extracted using an ultrasonic disrupter for 9 minutes. The extract is transferred to a separatory funnel containing water that has been adjusted to pH≥12. The sample is allowed to hydrolyze for one hour to convert the acid and ester forms of the herbicides to their salt forms. The solvent is discarded, and the aqueous phase, which contains the herbicides in their salt form, is acidified and extracted with diethyl ether. The extract is dried, concentrated, esterified with diazomethane, dissolved in MTBE, and analyzed by GC/ECD.

Sample Analysis Summary
The extracted methyl derivatives are analyzed by a GC equipped with dual capillary columns (different phases) connected to dual electron capture (EC) detectors, allowing simultaneous detection and confirmation of the target compounds. Quantitation is performed using the external standard calibration technique.

This SOP is based on the following methods: EPA 515.1, EPA 615, and EPA 8151A.

Example Analytical Sequence

Description	Comments
Blank	
Initial Calibration	
ICV	Second Source
Instrument Blank	
Laboratory Performance Check (LPC)	EPA 515.1 Only
Samples & Batch QC Items	
CCV	
Instrument Blank	
Samples & Batch QC Items	
CCV	
Instrument Blank	

The sequence continues until all samples have been analyzed or until the calibration verification fails the acceptance criteria. All sample extract analyses must be bracketed by acceptable verification standards.

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Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Method	Matrix	Routine Sample Container	Routine Sample Size	Minimum Sample Size	Chemical Preservation	Thermal Preservation	Dechlorination Agent	Holding Time
EPA 515.1	Water	1L amber glass	1L	500mL	None	0-6°C	80mg sodium thiosulfate	Extraction: 14 days from collection Analysis: 28 days from extraction
EPA 615	Water	1L amber glass	1L	500mL	None	0-6°C	None	Extraction: 7 days from collection Analysis: 40 days from extraction
EPA 8151A	Water	1L amber glass	1L	500mL	None	0-6°C	None	Extraction: 7 days from collection Analysis: 40 days from extraction
EPA 8151A	Soil	16oz soil jar	30g	15g	None	0-6°C	None	Extraction: 14 days from collection Analysis: 40 days from extraction

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Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration (ICAL) - 5-pt minimum	Initially, prior to sample analysis, and when acceptable CCV cannot be obtained	EPA 615: %RSD <=10%; r^2 >0.990 EPA 515.1 and 8151A: <20%RSD; r^2 >0.990	Refer to SOP SA-QA-16
2nd Source Initial Calibration Verification (ICV)	After Initial Calibration. (Quarterly, at a minimum, for EPA 515.1)	EPA 515.1: Percent difference <=20% EPA 615 and 8151A: Percent difference <=15% with no single analyte >45%	Refer to SOP SA-QA-16
Laboratory Performance Check (LPC)	EPA 515.1 Only: Daily, prior to sample analyses	See criteria in Attachment 6.	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards
Continuing Calibration Verification (CCV)	EPA 515.1: At the beginning and end of the analysis, and every 24 hours or 20 samples	Within ±20% of the true value	Refer to SOP SA-QA-16
	EPA 615: At the beginning of the analysis, and every 24 hours or 20 samples	Within ±10% of the true value	
	EPA 8151A: At the beginning and end of the analysis, and every 12 hours or 20 samples	Within ±15% of the true value; GME with no single analyte >45%	

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QC Item	Frequency	Criteria	Corrective Action
Calibration Blank (ICB/CCB)	After ICV and every CCV	<1/2 RL	Terminate the analysis, correct problem and reanalyze the previous samples.
Batch Definition	Up to 20 field samples, extracted together w/in 24-hour time period	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	<1/2 RL	Evaluate according to SOP SA-QA-17
Laboratory Control Sample (LCS)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Laboratory Control Sample Duplicate (LCSD)	One per batch, when insufficient sample provided for MS/MSD	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Low-Level Laboratory Control Sample (LLCS)	EPA 515.1 Only: One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Matrix Spike (MS)	EPA 515.1 and 615: 10% of samples prepared; i.e., 2 separate MS per batch EPA 8151A: One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Surrogate	All samples and batch QC items	Recoveries within MLG limits	Evaluate according to SOP SA-QA-17
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06 Note: Unsupervised work must not begin until acceptable IDOC is obtained.
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per analyte/method/matrix combination	Refer to SOP SA-QA-06	Refer to SOP SA-QA-06

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QC Item	Frequency	Criteria	Corrective Action
Reporting Limit Verification (RLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07
Method Detection Limit Study (MDL)	Upon method/instrument set-up, per analyte/method/matrix combination	Refer to SOP SA-QA-07	Evaluate according to SOP SA-QA-07
MDL Verification (MDLV)	Upon method/instrument set-up, per analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for non-DOD ELAP)	Refer to SOP SA-QA-07	Evaluate according to SOP SA-QA-07
Retention Time Window Determination	Annually	Refer to SOP SA-QA-08	Refer to SOP SA-QA-08

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Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling

Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log

A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives.

Preventive Maintenance

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE	
EQUIPMENT ITEM	**SERVICE LEVEL**
Water	Change the water in the water bath, recommended weekly. Add 1-2 drops of Clear Bath to prevent bacteria and algae growth.
K-D apparatuses	Inspect periodically for leaks and cracks. Leaks will allow the infiltration of water into the extract and compromise the entire extraction procedure.
Snyder Columns	Inspect frequently. The balls in the condenser will sometimes stick, causing pressure from the evaporating solvent to build up and spew the extract out of the top of the column. Wetting the column with a small volume of solvent will help to keep the balls from sticking.

Note: Glassware with leaks, cracks, and broken joints must be repaired or replaced.

Note: If the herbicide blank is contaminated, clean the diazomethane generator tubing and vessels with methylene chloride, methanol, and diethyl ether, in that order, and purge the apparatus with nitrogen to dry. Replace the Teflon tubing and vessels if the solvent cleaning does not improve the blank.

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LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Guard Column/Injector							X	Change sleeve and cut front of guard column, recommended daily
Septum							X	Replace , recommended daily
Splitless Disc							X	Replace , recommended daily
Autosampler							X	Syringe cleaned or replaced as needed
Column							X	Change column

D = daily; W = Weekly; M = monthly; Q = Quarterly; SA = semi-annually; A = annually; AN = as needed

Troubleshooting

Troubleshooting should be documented as outlined above. If possible, troubleshooting is best performed in a step-wise manner to systematically isolate instrument components. Refer to the instrument manufacturer's guides for specific information and strategies. Enlist assistance from technical and/or department management as needed.

Contingency Plan

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to ensure optimal instrument functioning. An extensive spare parts inventory is maintained for routine repairs. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

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Attachment 5:
Herbicide Molecular Weights and Correction Factors

Herbicide acid	MW_{acid}	$MW_{ester/ether}$	Correction factor
2,4-D	221.04	235.07	0.940
Dalapon	142.97	157.00	0.911
2,4-DB	249.09	263.12	0.947
Dicamba	221.04	235.07	0.940
Dichloroprop	235.07	249.09	0.944
Dinsoeb	240.22	254.24	0.945
MCPA	200.62	214.65	0.935
MCPP	214.65	228.67	0.939
2,4,5-TP(Silvex)	269.51	283.54	0.951
2,4,5-T	255.48	269.51	0.948
DCAA	205.04	219.07	0.936
Picloram	241.48	255.51	0.945
Pentachlorophenol	266.35	280.37	0.950
4-Nitrophenol	139.11	153.14	0.908
3,5-Dichlorobenzoic Acid	191.01	205.04	0.932
Acifluorfen	361.66	375.68	0.963
Chloramben	206.03	220.05	0.936
Bentazon	240.28	254.31	0.945

Example Calculation:

$$CF(2,4-D) = \frac{W_{acid}}{W_{ester/ether}} = \frac{221.04}{235.07} = 0.940$$

If the standard is expressed as mass of ester per volume, convert the concentration to the acid form by multiplying by the correction factor (CF).

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Attachment 6:
EPA 515.1 Laboratory Performance Check (LPC) Evaluation Criteria

Test	Analytes	Concentration (ug/mL)	Criteria
Sensitivity	Dinoseb	0.004	S/N>3
Chromat performance	4-nitrophenol	1.6	0.70<PGF<1.05
Column performance	3,5-Dichlorbenzoic acid	0.6	Resolution >0.4
	4-nitrophenol	1.6	

The sensitivity of the instrument is measured by determining the signal to noise ratio of dinoseb. The signal to noise ratio must be greater than 3 in order to analyze samples.

S/N = a ratio of peak signal to baseline noise

Where:
S = peak signal – measured as height of peak
N = baseline noise – measured as maximum deviation in baseline (in units of height) over a width equal to the width of the base of the peak

The chromatographic performance is measured by determining the Peak Gaussian Factor (PGF) of 4-nitrophenol. The Peak Gaussian Factor (PGF) is a mathematical representation of the peak shape. The closer to 1 the PGF is the more "normal" or "bell-shaped" the curve is. The PGF must be between 0.70 and 1.05 in order to analyze samples.

$$PGF = \frac{1.83 \otimes W_1}{W_2}$$

Where:
W_1 = the peak width at 1/2 the height (in seconds)
W_2 = the peak width at 1/10 the height (in seconds)

The column performance is measured by determining the resolution between 3,5-Dichlorobenzoic acid and 4-nitrophenol. Resolution (R) is a measure of the degree of separation of two peaks under specific chromatographic conditions and must be greater than 0.4 in order to analyze samples.

$$R = \frac{t}{W_{avg}}$$

Where:
t = the difference in elution times between the two peaks
W_{avg} = the average peak width of the two peaks (measurements taken at baseline)

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Attachment 7:
Maximum Contaminant Levels (MCL)

Primary Drinking Water Regulations		
Contaminant	**MCLG (mg/L)**	**MCL (mg/L)**
2,4-D	0.07	0.07
Dalapon	0.2	0.2
Dinoseb	0.007	0.007
Pentachlorophenol	0	0.001
Picloram	0.5	0.5
2,4,5-TP (Silvex)	0.05	0.05

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Attachment 8:
Glassware Cleaning

ZYMARK TUBE AND CLLE ROUNDBOTTOM FLASK CLEANING PROCEDURES

PPE: **Lab coat**
Eye protection
Kevlar gloves or equivalent

1. Note the condition of the Zymark tube or receiving flask. If heavily contaminated, do not place into the sink. Keep this glassware separate and contact the supervisor or Department Manager to determine the best course of action to clean the glassware.

   It is important to segregate heavily contaminated glassware from use until verified clean by the analysis of a method blank. Discard if the condition of the glassware cannot be verified or if the glassware is obviously not salvageable.

2. Rinse each tube or flask thoroughly with water and discard down the sink drain.

3. Fill dishpan with hot water and add about ¼ cup of FL-70 detergent per gallon of water.

4. For Zymark tubes, use a small brush to clean the tip of the tube and a larger brush to clean the walls of the tube.

   For receiving flasks, use a brush that will allow you to scrub the inside walls of the flask.

5. Rinse each tube and flask thoroughly a minimum of three times with hot tap water until no traces of soap are present in the tube. It is important to remove all traces of soap at this point.

6. Rinse each tube and flask thoroughly with acetone and place on covered counter or rack to dry.

   Discard acetone rinses down the sink drain with the cold tap water running.

7. Rinse each tube with a small aliquot of methylene chloride and place on covered counter or rack until ready for use.

   Discard methylene chloride in the satellite waste container designated for chlorinated waste.

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Attachment 9
Florisil Clean-up

- Place a small plug of glass wool into a 5 mL disposable glass pipette. Tare the pipette, and measure 1 g of activated Florisil into the pipette.
- Apply 5 mL of 5% methanol in MTBE to the Florisil. Allow the liquid to just reach the top of the Florisil. In this and subsequent steps, allow the liquid level to just reach the top of the Florisil before applying the next rinse, however, do not allow the Florisil to go dry. Discard eluate.
- Apply 5mL methylated sample to the Florisil leaving silicic acid in the tube. Collect eluate in K-D tube.
- Add 1mL of 5% methanol in MTBE to the sample container, rinsing walls. Transfer the rinse to the Florisil column leaving silicic acid in the tube. Collect eluate in a K-D tube. Repeat with 1 mL and 3 mL aliquots of 5% methanol in MTBE, collecting eluates in K-D tube.
- If necessary, dilute eluate to 10 mL with 5% methanol in MTBE.
- Seal the vial and store in a refrigerator if further processing will not be performed immediately.

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18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial, grammatical, and formatting changes made. Boilerplate text added.
- Added note that unsupervised work must not begin until acceptable IDOC is obtained. Attachment 3
- Added section on troubleshooting. Attachment 4
- Clarified requirements and frequency for RLVs, MDL Studies, and MDLVs to be consistent with SOP SA-QA-07 and to include the quarterly frequency as defined by DOD. Section 12.1 - 12.3 and Attachment 3
- Added section to describe analytical data system, software, and hardware. Section 6.2
- Added note that if an LCS and LCSD are performed, both QC items must be evaluated and reported. Acceptable recoveries (as well as %RPD) for both LCS and LCSD are required. Section 9.1.1
- Added note that some programs and agencies do not allow the use of quadratic curves and to refer to the Project Requirement Summary and/or Project Plan to determine if this curve type is prohibited. Section 9.2.2.1
- Added reference to TALS Historical Data Tracker feature. Section 11.1.7
- Added requirement to spike sample bottle with surrogate and spike mixes prior to any sample manipulation steps (i.e., pouring sample into separatory funnel apparatus). Section 10.1.2 (Corporate Internal Audit Finding, May 2010)

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SULFIDE: TITRIMETRIC PREPARATION AND ANALYSIS

(Total and Acid Soluble)

(Methods: EPA 376.1, EPA 9030B, and EPA 9034 and SM4500-S^{2-} F)

Approvals (Signature/Date):

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1.0 Scope and Application

This SOP gives the procedures for the determination of total sulfide in water by titration, and the determination of acid soluble sulfides in water and soil that have undergone the EPA 9030B distillation procedure (via MicroDist) followed by titration.

The reporting limits (RL) and the accuracy and precision criteria associated with this procedure are provided in the LIMS Method Limit Groups (MLGs).

This SOP was written by and for TestAmerica's Savannah laboratory.

2.0 Summary of Method

2.1 Sample Preparation

Total Sulfide: Treat the sample with zinc acetate and sodium hydroxide. The sulfide is precipitated as zinc sulfide. The precipitate is captured by centrifugation or filtration and reconstituted in reagent water.

Acid Soluble Sulfides (i.e., via distillation): An aliquot of the sample is added to the sample cup. 2mL of trapping solution (zinc acetate form) is added to the sample tube. A 0.45mL portion of releasing agent (H_2SO_4) is added to the sample cup and the distillation apparatus is immediately assembled. The samples are added to the distillation block that has been pre-heated to 120°C. The sample is heated for 30 minutes. The liberated hydrogen sulfide is swept into a scrubber solution containing zinc acetate. The presence of sulfide is evidenced by a white flocculation, zinc sulfide, in the scrubber solution. The acid soluble fraction includes dissolved hydrogen sulfide, unionized hydrogen sulfide, and acid soluble metal sulfides.

2.2 Sample Analysis

Sulfide is oxidized to sulfate in the presence of an excess of standardized iodine in an acidic medium. The mass of sulfide present in a sample is proportional to the amount of iodine required to oxidize the sulfide to sulfate. The excess iodine is back titrated with standardized sodium thiosulfate. The addition of starch indicator near the endpoint provides a clear endpoint.

The MicroDist distillate (processed for acid soluble sulfide analysis) is titrated in the same manner as samples processed for total sulfide. These solutions are basic and may require additional 6N HCl to bring the pH into the proper range for the titration. Samples that have undergone the preliminary preparation steps generally do not have matrix interferences or require zinc acetate separation or aluminum chloride flocculation.

This SOP is based on the following methods: EPA 376.1, EPA 9030B, EPA 9034, and SM4500-S^{2-} F. Note: Based on the 2007 Method Update Rule, EPA Method 376.1 is not approved for NPDES work. Standard Methods 4500-S^{2-} F is the approved NPDES method.

3.0 Definitions

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Refer to the Glossary Section of the *Quality Assurance Manual* (QAM) for a complete listing of applicable definitions and acronyms.

4.0 Interferences

4.1 Procedural Interferences

4.1.1 Interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus and can make identification and/or quantification of the target analytes difficult.

4.1.2 All sample collection containers are single-use disposable containers which limits the potential for contamination. All non-disposable labware must be scrupulously cleaned in accordance with the posted Labware Cleaning Instructions to ensure it is free from contaminants and does not contribute artifacts.

4.1.3 High purity reagents and solvents are used to help minimize interference problems. Hydrochloric acid and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

4.1.4 Instrument and/or method blanks are routinely used to demonstrate all reagents and apparatus are free from interferences under the conditions of the analysis.

4.1.5 Aqueous samples must be collected with a minimum of aeration to avoid the oxidation of sulfide to certain sulfur compounds that are not detected by this method.

4.1.6 Highly colored samples may impair the endpoint determination. Color may be diluted out by the addition of Reagent water (which will not affect the titration), or the sulfide can be precipitated with ZnAc and NaOH.

4.1.7 If the starch indicator is added too early in the titration, the iodine will bind with the starch and the titration will yield high bias results. The starch indicator must be added when a pale yellow color remains.

4.1.8 Reducing substances such as thiosulfate, sulfite and various organic compounds interfere with the iodometric titration by reacting with the iodine

4.2 Matrix Interferences

4.2.1 Matrix interferences may be caused by contaminants that are co-extracted from the sample matrix.

4.2.2 Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of analytes. As such, samples known to be clean should be analyzed first. To prevent carryover into subsequent samples, analysis of reagent blanks may be needed after the analysis of a sample containing high concentrations of analytes.

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4.2.3 Sulfite, thiosulfate, and hydrosulfite in concentrations which exceed 10mg/L decompose in acid to form sulfur dioxide which will be adsorbed in the zinc acetate scrubber solution. Sulfur dioxide will react with the iodine to yield false positive results. The addition of formaldehyde to the scrubber solution will prevent the sulfur dioxide from reacting with the iodine.

4.2.4 If a substantial amount of solids are present, they may interfere with the stir bar during the reaction time, causing low recoveries due to insufficient stirring.

5.0 Safety

Employees must abide by the policies and procedures in the TestAmerica Environmental Health and Safety Manual (EHSM), the TestAmerica Savannah Addendum to the EHSM, and this document.

This procedure may involve hazardous materials, 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 to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous.

The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested may contain hazardous chemical compounds or biological organisms. The analyst must, at a minimum, wear protective clothing (lab coat), eye protection (safety glasses or face shield), disposable nitrile gloves, and closed-toe, nonabsorbent shoes when handling samples.

The distillation units operate at elevated temperatures. The analyst must be aware of the location of the elevated temperature and cool the unit to room temperature before performing any maintenance. The analyst must wear the proper heat resistant gloves when handling the hot distillation tubes.

5.1 Specific Safety Concerns or Requirements

Sodium hydroxide is a severe corrosive. Skin contact can cause irritation or severe burns and scarring. Contact with the eyes can instantly cause irritation, burns, permanent vision impairment or blindness. Contact will destroy unprotected clothing.

Acetic acid is a corrosive. Contact with concentrated acetic acid can cause damage to the skin and eyes. Inhalation of concentrated vapors may cause damage to the lining of the nose, throat, and lungs.

Sulfuric acid is an oxidizer, a corrosive, a poison, and is reactive. Contact with the skin can cause severe burns, redness, and pain. Acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage. Contact will destroy unprotected clothing.

Hydrochloric acid is extremely hazardous as an oxidizer, a corrosive, a poison, and is reactive. It must always be handled under a properly functioning fume hood. It has a strong suffocating odor and inhalation of the vapors can cause coughing, choking,

irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage. Contact will destroy unprotected clothing.

Hydrogen sulfide (H_2S) gas is extremely poisonous. Exposure to large amounts of hydrogen sulfide gas can cause nausea, headaches, diarrhea, and even death. Although very high levels of hydrogen sulfide rarely occur in environmental samples, the analyst must be careful when handling these potentially dangerous samples.

The odor threshold for hydrogen sulfide is between 0.025ug/L and 0.25ug/L. This means you will smell hydrogen sulfide gas (a rotten egg smell) at levels that are not considered toxic, only bothersome. If the "rotten egg" smell is present when the sample is opened, the analysis of the sample should take place under a ventilation hood, or at a minimum, in a well ventilated area. Do not perform this analysis alone or in an isolated area-make sure that another lab employee is nearby.

The employee needs to follow all guidelines for glassware handling. Hand protection must be utilized when trying to separate ground glass fittings. Latex gloves do not provide protection from cuts from glassware.

5.2 Primary Materials Used

The following is a list of the materials used in this procedure, which have a serious or significant hazard rating, and a summary of the primary hazards listed in their MSDS.

NOTE: This list does not include all materials used in the procedure. A complete list of materials used in this procedure can be found in the Reagents and Standards Section and the Equipment and Supplies Section of this SOP

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. Electronic copies of MSDS can be found using the "MSDS" link on the Oasis homepage, on the EH&S webpage on Oasis, and on the QA Navigator.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Acetic Acid	Corrosive Poison Flammable	10ppm 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.
Formaldehyde	Poison	0.75ppm TWA	Inhalation of vapors may cause respiratory irritation leading to frequent bronchial infection. Eye contact causes redness, watering, and itching. Skin contact causes itching, scaling, and reddening or blistering.

Material	Hazards	Exposure Limit[1]	Signs and Symptoms of Exposure
Iodine	Poison Corrosive Oxidizer	0.1ppm Ceiling	Vapors severely irritate and can burn the mucous membranes and respiratory tract. Liquid contact may cause blistering burns, irritation, and pain. Vapors may be severely irritating to the skin. Vapors are severely irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Hydroxide	Corrosive	$2mg/m^3$ TWA	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Sulfide	Corrosive	10ppm TWA 15ppm STEL	Will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	$1mg/m^3$ TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Hydrochloric Acid	Corrosive Poison	5ppm Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

[1]Exposure limit refers to the OSHA regulatory exposure limit.

Note: Always add acid to water to prevent violent reactions.

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6.0 Equipment and Supplies

6.1 Equipment and Instrumentation

Analytical Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Top-loading Balance – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Thermometers – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

Centrifuge

10mL burette with 0.02mL increments – Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*

6.2 Lab Supplies

Volumetric Containers – various sizes; Class A, where applicable. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*.

Mechanical Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*.

Disposable Graduated Pipettes – various sizes. Verify in accordance with SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*.

pH paper (narrow range)

Lead Acetate (PbAc) Paper

Disposable eyedroppers

Stir Plate

Teflon Stir Bars

250mL and 500mL Beakers

Parafilm

Suction bulb

Desiccator

50mL disposable centrifuge tubes

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Detergent – used for washing non-disposable labware.

6.3 Sample Collection Containers

All sample collection containers are single-use disposable containers which limits the potential for contamination.

The routine sample collection containers supplied by the laboratory are purchased with a Certificate of Analysis attesting to purity and are as follows:

Water Samples: 250mL plastic, containing 2N zinc acetate and NaOH

Soil Samples: 4oz glass containers

7.0 Reagents and Standards

7.1 Expiration Dates

Expiration dates (time from initial use or receipt to final use) for standard and reagent materials must be set according to the guidance in this SOP. Note: These are maximum expiration dates and are not to be considered an absolute guarantee of standard or reagent quality. Sound judgment must be used when deciding whether to use a standard or reagent. If there is doubt about the quality of a standard or reagent material, a new material must be obtained or the standard or reagent material verified. Data quality must not be compromised to extend a standard's life – i.e., when in doubt, throw it out.

The expiration date of any standard or reagent must not exceed the expiration date of the standard or reagent that was used to prepare it; that is, the "children may not outlive the parents".

Unless listed elsewhere in this SOP, the expiration dates given below apply.

7.1.1 The expiration date for unopened standards and reagents is the manufacturer's expiration date.

7.1.2 The expiration date for opened stock reagents is the manufacturer's expiration date or 5 years from the date opened, whichever is sooner.

7.1.3 The expiration date for prepared reagents is 6 months from the date prepared or the expiration date of the parent reagent, whichever is sooner.

7.2 Reagents

Reagents must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures.*

Hydrochloric acid and sulfuric acid must be verified prior to use in accordance with the TestAmerica Solvent Lot Testing Program.

Unless otherwise listed, all reagents are stored at room temperature.

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7.2.1 Blank Matrix – Ottawa sand; Used for the preparation of soil QC samples

7.2.2 Laboratory Reagent Water – ASTM Type II

7.2.3 Glacial Acetic Acid (CH_3COOH) – reagent grade
LIMS Name: aceticacid
Storage: Store in a cool, dry, ventilated area. Protect from heat, flame, and incompatibles.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

7.2.4 Zinc Acetate [$Zn(CH_3COO)_2 \cdot 2H_20$] – reagent grade
Storage: Store in a cool, dry, ventilated area away from incompatibles.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

7.2.5 Zinc Acetate (2N) – Dissolve 44g of zinc acetate in 80mL of reagent water in a 100mL volumetric flask. Dilute to 100mL with reagent water. Transfer this solution to a glass or plastic container for storage.
LIMS Name: 2N Znac
Storage: Room temperature
Expiration: 1 year from preparation date

7.2.6 Zinc Acetate (0.5M) – Dissolve 110g zinc acetate in 800mL reagent water. Add 1mL of concentrated HCl and dilute to 1L with reagent water. Transfer this solution to a glass or plastic container.
LIMS Name: 0.5M Znac
Storage: room temperature
Expiration: 1 year from preparation date

Note: HCl is added to this reagent to prevent the precipitation of zinc hydroxide simultaneously with the zinc sulfide.

7.2.7 Sodium Hydroxide (NaOH) – reagent grade.
LIMS Name: Sod hydrox
Storage: Store tightly sealed in a cool, dry, ventilated area. Protect from moisture, heat, and incompatibles.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

7.2.8 Sodium Hydroxide (6N) – In a 100mL volumetric flask, dissolve 24.0g NaOH in 80mL reagent water. Place a stir bar in the volumetric flask, and stir the solution on a stir plate until all of the NaOH has dissolved. Remove the stir bar and dilute to 100mL with reagent water. Transfer this solution to a plastic container for storage.

CAUTION: Heat will be evolved as the sodium hydroxide is dissolved in the water. Sodium hydroxide solutions are caustic and will cause skin burns and destroy unprotected clothing.

LIMS Name: 6N NaOH
Storage: Store tightly sealed in a cool, dry, ventilated area. Protect from moisture, heat,

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and incompatibles.
Expiration: 1 year from preparation date

7.2.9 Formaldehyde (37% solution) – reagent grade
LIMS Name: Formaldehy
Storage: Store in a cool, dry, ventilated area. Protect from heat, flame, and incompatibles.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

7.2.10 Sulfuric Acid (H_2SO_4) – concentrated; reagent grade
LIMS Name: H2SO4Conc
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

7.2.11 Hydrochloric Acid (HCl) – concentrated; reagent grade
LIMS Name: HCl
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration ndate

7.2.12 Hydrochloric Acid (6N) – Under a ventilation hood, in a 1L glass beaker, place approximately 400mL of reagent water. Place the beaker on a stir plate. Place a large stir bar in the beaker and begin stirring the water. Slowly add 400mL of concentrated HCl. Allow this solution to mix until cooled to room temperature. Carefully transfer this solution to a glass or plastic container for storage.
LIMS Name: 6N HCl
Storage: Store in a cool, dry, ventilated storage area with acid resistant floors and good drainage. Store away from sunlight, heat, water, and incompatible materials.

7.2.13 MicroDist Releasing Agent (9M H2SO4 Solution)
LIMS Name: 9MH2SO4
Storage: Store in a cool, dry ventilated area
Expiration: 6 months from preparation date

Prepare the releasing agent by weighing out 150g of DI water on a top loading balance into a tared 500mL beaker in the fume hood. Slowly add 276g of concentrated H_2SO_4 to the water (30-40g at a time). Allow the solution to cool to room temperature and transfer to a plastic container.

7.2.14 MicroDist Trapping Solution (0.043M Zinc Acetate Solution)
Storage: Store in a cool, dry ventilated area
Expiration: 6 months from preparation date

Dissolve 8.78g of zinc acetate, 0.1g Conc. HCl (approx. one drop) and 43.2g of 37% Formaldehyde solution in 880g of DI water and mix.

7.2.15 Potassium Iodide (KI) – reagent grade
LIMS Name: pot.iodide

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Storage: Store in a cool, dry ventilated area.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

7.2.16 Starch Solution – reagent grade, commercially prepared. Transfer starch solution to a plastic squirt bottle.
LIMS Name: H2S Starch
Storage: Store in a cool, dry area.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

7.2.17 Potassium Iodate (KIO_3) – reagent grade
LIMS Name: pot.iodate
Storage: Store in a cool, dry, ventilated area. Protect from heat, flame, and incompatibles.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

7.2.18 Potassium Iodate Solution
LIMS Name: Pot.Iodate
Storage: Store in a cool, dry area.
Expiration: 1 week from preparation date

7.2.18.1 Dry 3-4g of KIO_3 at 180°C for a minimum of two hours. Allow to cool. Transfer to an airtight container, and store in a dessicator until needed for the standardization of the Sodium Thiosulfate Solution.

7.2.18.2 Using an analytical balance, weigh out 1.2 -1.5g of dried KIO_3, measured to the nearest 0.0001g. Quantitatively transfer the weighed KIO_3 to a 250mL volumetric flask, using several aliquots of reagent water to completely transfer the KIO_3. Dilute to volume with reagent water. Mix this solution and transfer to a glass or plastic container.

Calculate the normality of the KIO_3 as follows:

$$N(KIO3) = \frac{A}{35.67g/eq \otimes 0.25L}$$

Where:
A = weight of KIO_3 (in grams)
35.67g/eq = equivalent weight of KIO_3

Record the normality of the KIO_3 on the Standardization Log.

7.2.19 Sodium Thiosulfate ($Na_2S_2O_3$) Solution (0.025N) – commercially prepared
Storage: Store in a cool, dry ventilated area.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

Note: The 0.025N solution must be standardized weekly against the Potassium Iodate Solution as detailed below.

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7.2.19.1 Rinse a 10mL burette with the Sodium Thiosulfate Solution ($Na_2S_2O_3$). Fill the burette with the $Na_2S_2O_3$.

7.2.19.2 Weigh approximately 3.0g KI (potassium iodide) into each of three 250mL Erlenmeyer flasks. Add approximately 50mL reagent water and a stir bar to each flask. Begin stirring this solution. Add 2mL 6N HCl to the KI solution in each flask. Mix this solution until the KI dissolves.

Treat each flask individually from this point on.

7.2.19.3 Using a volumetric pipette, transfer 2.5mL of the KIO_3 solution to the KI-acid solution.

7.2.19.4 Titrate with 0.025N $Na_2S_2O_3$ to a pale yellow color. Add 1mL of starch indicator solution (the solution will turn blue) and titrate drop-wise to a colorless endpoint. Record the $Na_2S_2O_3$ titer in the Standardization Log.

Note: It is critical the analyst titrate to the palest yellow color distinguishable BEFORE adding the starch indicator otherwise the starch will bind with the excess iodine and cause biased high results.

Titrate the other two standardization aliquots, recording all three titers in the log.

7.2.19.5 Calculate the normality (N) of the $Na_2S_2O_3$ as follows:

$$N = \frac{A \otimes B}{V}$$

Where:
A = mL of KIO_3 titrated
B = N of KIO_3
V = mL $Na_2S_2O_3$ required to reach the endpoint

7.2.19.6 Record the normality of each solution in the Standardization Log.

Calculate the average of the three standardization analyses. Use the average normality in the calculation of the normality of the Iodine Solution.

7.2.20 Sodium Thiosulfate ($Na_2S_2O_3$) Solution (0.00625N)
Storage: Store in a cool, dry ventilated area.
This solution is prepared diluting the 0.025N Sodium Thiosulfate 1:4 with DI water

7.2.21 Iodine (I_2) Solution (0.10N) – commercially prepared
LIMS Name: H2SIodine
Storage: Store tightly sealed in a cool, dry, ventilated area. Protect from reactive or combustible materials and sunlight.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

Note: This solution must be standardized weekly and whenever a new bottle is opened as detailed below.

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7.2.21.1 Rinse the 10mL burette with the standardized $Na_2S_2O_3$. Fill the burette with the standard $Na_2S_2O_3$ to prepare for titration.

7..2.21.2 Using a volumetric pipette, transfer 2.5mL of 0.10N I_2 to each of three 250mL Erlenmeyer flasks.

7.2.21.3 Add 2mL of 6N HCl and approximately 50mL of reagent water to each of the flasks.

7.2.21.4 Place the flask on a stir plate and add a stir bar. While stirring, titrate the iodide solution with the standardized $Na_2S_2O_3$ to a pale yellow color. Add approximately 1mL of the starch indicator solution, and titrate to a colorless endpoint.

Note: It is critical the analyst titrate to the palest yellow color distinguishable BEFORE adding the starch indicator otherwise the starch will bind with the excess iodine and cause biased high results.

Titrate each of the flasks containing the iodide solution and record the volume (mL) of $Na_2S_2O_3$ required for each standardization in the Standardization Log.

7.2.21.5 Calculate the normality (N) of the I_2 solution as follows:

$$N(I2) = \frac{A \otimes B}{V}$$

Where:
A = mL of standard $Na_2S_2O_3$
B = normality of standard $Na_2S_2O_3$
V = mL of I_2

Record the normalities determined for the I_2 along with the average normality of the iodine solution in the Standardization Log.

Use the average normality in the calculation of the sulfide concentration.

7.2.22 Dessicant – Drierite
LIMS Name: DriRight
Storage: Store in a cool, dry ventilated area.
Expiration: Unopened: Manufacturer's expiration date; Opened: Manufacturer's expiration date

7.3 <u>Standards</u>

Standards must be prepared and documented in accordance with SOP SA-AN-041: *Reagent and Standard Materials Procedures*. Certificates of analysis or purity must be received with all purchased standards, and scanned and filed in the Data Archival Folder on the G-drive.

Unless otherwise listed, all standards are stored at room temperature.

Sodium Sulfide Nonahydrate ($Na_2S{\cdot}9H_2O$) – reagent grade. This solid must be stored in a dessicator at all times.

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LIMS Name: sodsulfid
Storage: Dessicator
Expiration:
Unopened: Manufacturer's expiration date or five years from receipt
Opened: Manufacturer's expiration date or five years from receipt

Sulfide Stock Standard (approximately 10,000mg/L S) – In a 100mL volumetric flask, dissolve 7.51g of $Na_2S{\cdot}9H_2O$ in 80mL reagent water. Place a stir bar in the solution, and stir on a stir plate until the solid is dissolved. Remove the stir bar and dilute to 100mL with reagent water. Test the solution with narrow range pH paper. The pH must be >9. If the pH is >9, then additional NaOH is added until pH >9 is achieved.
LIMS Name: SulfideLCS
Storage: Room temperature, in 125mL plastic bottle
Expiration: Standardize weekly, re-prep every three months

Note: This stock solution must be standardized after preparation using the titration procedure given in Section 10. Transfer 0.25mL of the stock standard to a flask containing 2.5mL of 0.10N iodine and 2mL of 6N HCl. Perform the standardization in triplicate and use the average for the preparation of intermediate, spiking, and calibration standards.

8.0 Sample Collection, Preservation, Shipment, and Storage

Refer to Attachment 2 for a summary of bottles types, preservatives, and holding time requirements.

8.1 Aqueous Samples

Aqueous samples are routinely collected in 250mL plastic containers containing 2N zinc acetate and NaOH. Samples should be collected with zero headspace.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation and/or analysis. Samples must be prepared and analyzed within 7 days of collection.

NCMs must be initiated for samples collected in improper containers and containing improper or insufficient preservatives. NCMs must be initiated for samples that are received containing headspace.

8.1.1 Preservation Checks

8.1.1.1 Sulfide Verification

For each sample, upon sample receipt,
- Visually inspect the sample for a white precipitate indicating the presence of zinc sulfide (ZnS).
- Place a piece of lead acetate (PbAc) paper in a disposable medicine cup.
- Wet the PbAc paper with concentrated acetic acid.
- Pour a few drops of sample into the medicine cup and note the color change of the PbAc paper.

- If the PbAc paper remains white the sample is properly preserved with zinc acetate (ZnAc).
- If the PbAc paper turns black the sample contains un-precipitated sulfide. Initiate a Nonconformance Memo. Add a small aliquot of 2N ZnAc to the sample container. Shake the sample gently to mix the ZnAc with the sample. Allow the precipitate to settle. Check for the presence of sulfide again and repeat as necessary until all of the sulfide in solution has been precipitated.
- Record the approximate volume of 2N ZnAc added to the sample.

Note: To avoid cross-contamination, use a separate medicine cup and piece of pH paper per sample. Do not dip the PbAc paper into the sample container. The PbAc paper dye may bleed into the sample and affect sample results.

8.1.1.2 pH Verification

For each sample, upon sample receipt,
- Place a piece of pH paper in a disposable medicine cup.
- Pour a few drops of sample into the medicine cup and note the color change of the pH paper.
- If the pH is not greater than 9, initiate a Nonconformance Memo. Adjust the sample pH to >9 using 6N NaOH.

Note: To avoid cross-contamination, use a separate medicine cup and piece of pH paper per sample. Do not dip the pH paper into the sample container. The pH paper dye may bleed into the sample and affect sample results.

8.2 Soil Samples

Soil samples are routinely collected in 4oz glass containers. The soil container must be filled completely to avoid any exposure to air.

Samples must be iced at the time of collection and maintained at 4°C (less than 6°C but not frozen) until the time of preparation and/or analysis. Samples must be analyzed within 14 days of collection.

NCMs must be initiated for samples that are received containing headspace.

9.0 Quality Control

SOP SA-QA-17: *Evaluation of Batch QC Data* and the SOP Summary in Attachment 3 provide requirements for evaluating QC data.

9.1 Batch QC

Batch QC must meet the criteria given in Attachment 3 of this SOP.

A preparation / analysis batch consists of up to 20 environmental samples and the associated QC items analyzed together within a 24 hour period.

9.1.1 EPA Method 376.1 – Aqueous Samples

This method does not specify any QC items. The laboratory's minimum default QC items

required for each analytical batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD).

The routine container supplied for this method is a 250mL container. 250mL is required for analysis.

If there is insufficient sample to perform the required matrix spike(s), the LCS must be performed in duplicate (i.e., LCSD). An NCM must be initiated on all affected samples to denote this situation. Insufficient sample volume is defined as receiving less than a total of 750mL.

MRL LCS for DW
The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water samples, an LCS at the RL must also be included in the required batch QC.

9.1.2 Standard Methods 4500-S^{2-} F – Aqueous Samples
The minimum QC items required for each analytical batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), a matrix spike duplicate (MSD), and a sample duplicate.

The routine container supplied for this method is a 250mL container. 250mL is required for analysis. If there is insufficient sample to perform the required matrix spike(s) and/or sample duplicates, an NCM must be initiated on all affected samples to denote this situation and the LCS must be performed in duplicate (i.e., LCSD). Insufficient sample volume is defined as receiving less than a total of 750mL.

MRL LCS for DW
The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. Therefore, if analyzing drinking water samples, an LCS at the RL must also be included in the required batch QC.

9.1.3 EPA Methods 9030B and 9034 – Aqueous Samples
The minimum QC items required for each analytical batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate.

The routine container supplied for this method is a 250mL container. 250mL is required for analysis for titration only. 6mL is required for EPA 9030B distillation. If there is insufficient sample to perform the required matrix spike(s), an NCM must be initiated on all affected samples to denote this situation and the LCS must be performed in duplicate (i.e., LCSD). Insufficient sample volume is defined as receiving less than a total of 750mL for titration only and 20mL for EPA 9030B distillation.

9.1.4 EPA Methods 9030B and 9034 – Soil Samples
The minimum QC items required for each analytical batch are: a method blank, a laboratory control sample (LCS), a matrix spike (MS), and a matrix spike duplicate.

The routine container supplied for these methods is a 4oz container. 1.0g is required for analysis. If there is insufficient sample to perform the required matrix spike(s) and/or sample duplicates, an NCM must be initiated on all affected samples to denote this situation and the LCS must be performed in duplicate (i.e., LCSD). Insufficient sample

volume is defined as receiving less than a total of 5g.

9.2 Instrument QC

There are no instrument QC items associated with this procedure.

9.3 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP SA-QA-05: *Preventive and Corrective Action Procedures* the QC Summary Table in Attachment 3. SOP SA-QA-05 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures. Nonconformance Memos must be initiated to document all instances where QC criteria are not met and all departures from approved policies and procedures.

10.0 Procedure

10.1 Sample Preparation

Soil samples must be homogenized prior to preparation in accordance with SOP SA-QA-15: *Compositing, Homogenization, and Segregation of Samples.*

10.1.1 Total Sulfide Sample Preparation

Allow samples to come to room temperature before titration. No other sample preparation is required prior to titration unless samples are highly colored or interferences are present.

For highly colored samples and samples with known or suspected interferences, the sulfide must be separated from the interference as follows. The sample must have been properly preserved upon arrival in the lab. The sulfide in a properly preserved sample will be precipitated as zinc sulfide.

10.1.1.1 Draw a line on the sample container indicating the sample level in the container, using a water-proof marker.

10.1.1.2 Shake the sample container vigorously. Pour the sample into centrifuge tubes, cap, and centrifuge at 3/4 speed for approximately 3-5 minutes.

10.1.1.3 Decant the supernatant and discard. Add approximately 25-30mL of DI water to each centrifuge tube and shake vigorously to loosen the precipitate in the bottom of the centrifuge tube.

10.1.1.4 Pour the contents of each centrifuge tube back into the original sample container. Dilute the precipitate back to the volume of the original sample indicated by the black line on the sample container.

10.1.1.5 The prepared sample is titrated as in Section 10.3.

10.1.2 Acid Soluble Sulfide – MicroDistillation

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- Turn on MicroDist heater block and set to 120°C. Allow approximately 45 minutes for unit to come to temperature.
- Add the appropriate number of collector tubes to the tube rack with the M end facing up.
- Add 2mL of trapping solution to each tube.
- Cap off the tube by adding one membrane and one plastic cap to the top. Ensure that the membrane covers the tube all the way around the cap.
- Add the appropriate number of sample tubes to the sample rack.
- For liquids, dispense 6mL of sample into each sample tube. For soils, add 1.0g of sample to the tube and 5mL of DI water.

> **Note: For oily samples or other samples high in organics, it may be necessary to decrease the sample amount to 0.1-0.5g. These samples tend to cake up the hydrophobic membrane and allow undistilled sample to pass into the collector tube.**

- Add 0.45mL of the releasing agent to the sample tube. Immediately press the D end of the collection tube over the open end of the sample tube by hand.
- Place the assembly in the press, putting the sample tube through the hole in the white base. Before pressing, grip the collector tube at the break away point to keep the tube from shifting or cracking when the tube is pressed. Apply smooth constant pressure to the tube to complete the assembly. Press down until the stop ring on the sample tube meets the D end of the collector tube.

> **Note: the process of adding the releasing agent to tube assembly should be done one at a time since the sulfide is liberated by addition of acid.**

- Once all of the tubes have been assembled, they can be added to the block. Note: Heat resistant gloves must be used.
- Add each tube to the block ensuring that the stop ring on the collector tube is touching the heat block.
- Once all of the samples have been placed, set the timer for 30 minutes.
- When time is up, put on the heat resistant gloves again to remove the tubes. It is important to only remove one tube at a time. Once the first tube is removed, quickly disconnect the sample tube from the collection tube with a downward pulling and twisting motion. Put the collector tube cap side down into the collector tube rack.

> **Note: This process needs to be completed within approximately 4 seconds of removing the sample from the block to prevent "suck-back", a process where the rapid cooling of the sample causes the distilled sample to "suck back" into the sample tube by rupturing the membrane. If this occurs the sample must be re-prepped.**

- The sample tube and hot liquid can be collected in a plastic bin and thrown away.
- Once all of the tubes are disassembled, allow the distillates to cool for approximately 10 minutes.
- Hold the collector tube horizontally in your hands and roll the distillate around in the collector tube to collect stray drops of distillate.
- Hold the tube vertically with the cap side down and flick the tube with your finger if needed to collect the last drops.

- Grasp the D end of the tube with the other hand and pull the tube towards you and then away from you to complete the break in the tube. Now you can bring the distillate up to a final volume of 6mL with DI water.
- The open end of the tube should be sealed with Parafilm until ready for analysis.
- The prepared sample is titrated as in Section 10.3.

10.2 QC Sample Preparation

All QC samples are prepared in the same manner as samples using the appropriate steps from Section 10.1.

10.3 Analysis

10.3.1 The default procedure is to include QC items (method blank, LCS, MS/MSD, and SD) in determining the maximum number of samples in the batch.

10.3.2 Rinse the 10mL burette with the standardized $Na_2S_2O_3$. Fill the burette with the $Na_2S_2O_3$ to prepare for titration. Note: 0.025N standardized $Na_2S_2O_3$ is used for EPA 376.1 and SM4500-S^2-F. The 0.00625N titrant is used for EPA 9030/9034 micro-distilled samples.

10.3.3 For EPA 376.1 and SM4500-S^2-F, use a volumetric pipette to transfer 2.5mL of standardized I_2 solution into a 500mL or 1000mL glass beaker (beaker size is dependent upon sample size). Place this solution on a stir plate. Add a large stir bar.

For EPA 9030/EPA 9034 distilled samples, use a volumetric pipette to transfer 1.0mL of standardized I_2 solution into a 250mL glass beaker containing 100mL of DI water. Place this solution on a stir plate. Add a 1 inch stir bar.

10.3.4 Add 2mL of 6N HCl.

10.3.5 Using a permanent marker, mark a line on the sample bottle at the liquid level BEFORE removing any sample.

10.3.6 Remove the beaker from the stir plate.

For EPA 376.1 and SM4500-S^2-F, pipette the entire sample under the surface of the Iodine/HCl mixture using an automated pipetter and 50mL disposable pipettes. Rinse the sample container with DI water and pour washings in the iodine-acid mixture also. Place the beaker back on the stir plate and continue stirring.

For EPA 9030/EPA 9034 distilled samples, pipette the 6mL of distillate under the surface of the Iodine/HCl mixture.

10.3.7 Note: If only one sample container was submitted for sulfide analysis, a sample aliquot may be analyzed instead of the entire sample. If this is the case, the sample must be shaken well to mix the sample liquid with the precipitated sulfide.

10.3.8 If the solution turns colorless upon the addition of the sample, check the pH of the solution with pH paper. Place a drop of the sample on the pH paper. Do not dip the pH paper into the sample. If the pH is greater than 2, add 6N HCl in 2mL increments until the pH is less

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than 2. If the pH is less than 2 and the solution has turned colorless, add 0.10N I_2 in 1mL increments until an orange color persists.

10.3.9 Turn on the stir plate to allow for mixing during titration.

10.3.10 Titrate the sample solution with appropriate $Na_2S_2O_3$ to a pale yellow color.

10.3.11 Add approximately 1mL of starch indicator. The solution will turn blue.

Note: It is critical that the analyst titrate to the palest yellow color distinguishable BEFORE adding the starch indicator solution because the starch will bind with the iodine and cause biased high results.

The titration needs to be slow particularly around the pale yellow and blue to clear determination. Once the endpoint is observed, wait one minute to ensure the blue color does not re-appear.

10.3.12 Continue to titrate drop-wise until the sample solution turns colorless. Record the titer in the TALS AD batch.

10.3.13 Fill the sample bottle with tap water to the previously marked level. Measure the volume of water in the sample container with a graduated cylinder. The volume of water measured will equal the volume of sample actually titrated if the entire sample aliquot was measured. Record the sample volume titrated in the TALS AD batch.

11.0 Calculations / Data Reduction

11.1 Data Reduction

Data must be evaluated in accordance with SOP SA-QA-02: *Data Generation and Review*.

11.1.1 MS/MSD Evaluation

If the concentration of a target analyte in the un-spiked (native) sample is more than four times the theoretical concentration of the matrix spike, the recovery is not reported and the data is flagged.

11.1.2 Historical Data

Many of the laboratory's clients submit samples for repeat monitoring purposes. Prior to analysis, verify LIMS Worksheet Notes and/or use the Historical Data tracker feature to determine if historical data is available for review.

11.2 Calculations

11.2.1 The calculations associated with batch QC determinations are given in SOP SA-QA-17. Applicable calculations include accuracy (% recovery) and precision (%RPD).

11.2.2 The calculation to determine final concentration is given as follows:

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Liquids

$$\frac{mg\ S}{L} = \frac{(A \otimes B) - (C \otimes D)}{V} \otimes \frac{32.06\ mg\ S}{2\ meq\ I_2} \otimes \frac{1000\ mL}{1\ L}$$

Where:
A = mL of standardized I_2
B = N of I_2
C = mL of standardized $Na_2S_2O_3$
D = N of $Na_2S_2O_3$
V = volume of sample (mL)

Soils

$$\frac{mg\ S}{kg}, dw = \frac{(A \otimes B) - (C \otimes D)}{\frac{W \otimes solids}{FV} \otimes Vt} \otimes \frac{32.06\ mg\ S}{2\ meq\ I_2} \otimes \frac{1000\ g}{1\ kg}$$

Where:
A = mL of standardized I_2
B = N of I_2
C = mL of standardized $Na_2S_2O_3$
D = N of $Na_2S_2O_3$ from Section
W = weight of sample (g)
solids = (percent solids)/100
FV = final volume of the distillate (mL)
Vt = volume of distillate titrated (mL)

12.0 Method Performance

12.1 Reporting Limit Verification (RLV)

At a minimum, RLVs must be performed initially upon method set-up in accordance with SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*.

For analytes and methods certified by DOD ELAP, RLVs must also be performed quarterly thereafter. For analytes and methods certified by NELAC, RLVs must also be performed annually thereafter.

12.2 Method Detection Limit (MDL) Study

Method detection limits as generated in accordance with 40CFR Part 136 Appendix B are not applicable to this procedure. The reporting limit is based on the lowest discernable value achievable by the instrument/labware.

12.3 Method Detection Limit Verification (MDLV)

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Method detection limits as generated in accordance with 40CFR Part 136 Appendix B are not applicable to this procedure. The reporting limit is based on the lowest discernable value achievable by the instrument/labware.

12.4 QC Limit Generation, Control Charting, and Trend Analysis

The control limits for the batch QC items (e.g., LCS, MS/MSD, SD) for this procedure are specified in the reference method and cannot be broadened; therefore, the laboratory defaults to the method-defined limits and does not utilize in-house or laboratory-derived limits for the evaluation of batch QC items.

Although the laboratory must default to the method-defined QC limits, control charting is a useful tool and is performed to assess analyte recoveries over time to evaluate trends. Control charting must be performed periodically (at a minimum annually) in accordance with SOP SA-QA-17: *Evaluation of Batch QC Data*.

12.5 Demonstrations of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP SA-QA-06: *Training Procedures*.

Prior to performing this procedure unsupervised, each new analyst who performs this analysis must demonstrate proficiency per method/analyte combination by successful completion of an initial demonstration of capability. The IDOC is performed by the analysis of 4 consecutive LCSs that meet the method criteria for accuracy and precision. The LCSs must be from a second source than that used to prepare the calibration standards. The IDOC must be documented on the IDOC Form shown in SOP SA-QA-06 with documentation routed to the QA Department for filing.

Annual continuing demonstrations of capability (CDOCs) are also required per analyst per method/analyte combination. The CDOC requirement may be met by the consecutive analysis of four LCS all in the same batch, by the analysis of four LCS analyzed in four consecutive batches (in different batches on different days), via acceptable results on a PT study, or analysis of client samples with statistically indistinguishable results when compared to another certified analyst. The CDOC must be documented and routed to the QA Department for filing.

12.6 Training Requirements

All training must be performed and documented in accordance with SOP SA-QA-06: *Training Procedures*.

Note: The SOPs listed in the Reference/Cross-Reference Section are applicable to this procedure. All employees performing this procedure must also be trained on these SOPs, and/or have a general understanding of these procedures, as applicable.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (e.g., examining recycling options, ordering chemicals based on quantity

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needed, preparing reagents based on anticipated usage and reagent stability, etc.). Employees must abide by the policies in Section 13 of the Environmental Health and Safety Manual and the TestAmerica Savannah Addendum to the EHSM.

This procedure has been evaluated for opportunities to minimize the waste generated. Where reasonably feasible, pollution control procedures have been incorporated.

14.0 Waste Management

Waste management practices must be conducted consistent with all applicable federal, state, and local rules and regulations. All waste (i.e., excess reagents, samples, and method process wastes) must be disposed of in accordance with Section 9 of the TestAmerica Savannah Addendum to the EHSM. Waste description rules and land disposal restrictions must be followed.

14.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Acidic residue from the distillation flasks must be neutralized before disposal into the sewer system.

- Non-hazardous acidic and alkaline wastewater and samples must be neutralized before disposal into the sewer system.

15.0 References / Cross-References

- SOP SA-AN-041: *Reagent and Standard Materials Procedures*
- MicroDist Operation and Application Manual Rev23May02
- SOP SA-AN-100: *Laboratory Support Equipment (Verification and Use)*
- SOP SA-QA-02: *Data Generation and Review*
- SOP SA-QA-05: *Preventive and Corrective Action Procedures*
- SOP SA-QA-06: *Training Procedures*
- SOP SA-QA-07: *Determination and Verification of Detection and Reporting Limits*
- SOP SA-QA-15: *Homogenization, Compositing, and Segregation of Samples*
- SOP SA-QA-17: *Evaluation of Batch QC Data*
- TestAmerica Savannah Quality Assurance Manual
- TestAmerica Environmental Health and Safety Manual (CW-E-M-001)
- TestAmerica Savannah Addendum to the Environmental Health and Safety Manual

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- *Standard Methods for the Examination of Water and Wastewater*; Online Edition; American Public Health Association: Washington, DC
  - SM4020: *Quality Assurance/Quality Control*
  - SM4500-S^{2-} F: *Sulfide, Iodometric Method*; 2000
- *Methods for Chemical Analysis of Water and Wastes*; U.S. EPA Office of Research and Development: Cincinnati, OH, March, 1983
  - EPA 376.1: *Sulfide (Titrimetric, Iodine)*; 1978
- *Test Methods for Evaluating Solid Waste, Third Edition On-line*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC
  - EPA 9030B: *Acid-Soluble and Acid-Insoluble Sulfides; Distillation*; Revision 2, December 1996
  - EPA 9030B: Titrimetric Procedure for *Acid-Soluble and Acid-Insoluble Sulfides*; Revision 0, December 1996

16.0 Method Modifications and Clarifications

16.1 This procedure may be modified to analyze other matrices (e.g., waste or tissue samples) based on the needs of the client. This will need to be arranged by the Project Manager at the initiation of the project. Wipe, waste, and tissue matrices are non-routine, and the laboratory is not currently NELAC certified for these matrices. The laboratory uses its routine soil RLs (converted for initial and final volumes, etc.), and soil QC limits to evaluate wipe, waste, and tissue samples. Soil DOCs can be used to satisfy analyst demonstrations of capability for these types of non-routine matrices. Ottawa sand is used as the blank matrix for tissue samples unless a "true" tissue matrix is required by the project.

16.2 The EPA Manual for the Certification of Laboratories Analyzing Drinking Water requires a LFB at the MRL to be performed each day. The laboratory meets this requirement by preparing an LCS at the RL in each batch of drinking water samples. The EPA DW Manual does not specify criteria for the low-level LCS; therefore, the laboratory defaults to 50-150%.

16.3 The laboratory has incorporated the minimum batch QC items as outlined in Section 9.1. Some additional QC items are routinely performed above those required in the reference methods (i.e., LCSD and MS/MSD) to satisfy common regulatory and/or client requests for precision data and/or to facilitate scheduling and data evaluation.

16.4 Based on the 2007 Method Update Rule, EPA Method 376.1 is not approved for NPDES work. Standard Methods 4500-S^{2-} F is the approved NPDES method.

17.0 Attachments

The following Tables, Diagrams, and/or Validation Data are included as Attachments:

Attachment 1: SOP Summary
Attachment 2: Sample Collection, Preservation, and Holding Time Table
Attachment 3: QC Summary
Attachment 4: Instrument Maintenance and Troubleshooting
Attachment 5: Gas Evolution Apparatus

Attachment 1:
SOP Summary

Sample Preparation Summary

Total Sulfide: Treat the sample with zinc acetate and sodium hydroxide. The sulfide is precipitated as zinc sulfide. The precipitate is captured by centrifugation or filtration and reconstituted in reagent water.

Acid Soluble Sulfides (i.e., via distillation): An aliquot of the sample is added to the sample cup. 2mL of trapping solution (zinc acetate form) is added to the sample tube. A 0.45mL portion of releasing agent (H_2SO_4) is added to the sample cup and the distillation apparatus is immediately assembled. The samples are added to the distillation block that has been pre-heated to 120°C. The sample is heated for 30 minutes. The liberated hydrogen sulfide is swept into a scrubber solution containing zinc acetate. The presence of sulfide is evidenced by a white flocculation, zinc sulfide, in the scrubber solution. The acid soluble fraction includes dissolved hydrogen sulfide, unionized hydrogen sulfide, and acid soluble metal sulfides.

Sample Analysis Summary

Sulfide is oxidized to sulfate in the presence of an excess of standardized iodine in an acidic medium. The mass of sulfide present in a sample is proportional to the amount of iodine required to oxidize the sulfide to sulfate. The excess iodine is back titrated with standardized sodium thiosulfate. The addition of starch indicator near the endpoint provides a clear endpoint.

The MicroDist distillate is titrated in the same manner as routine samples. Samples that have undergone the preliminary preparation steps generally do not have matrix interferences or require zinc acetate separation or aluminum chloride flocculation.

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Attachment 2:
Sample Collection, Preservation, and Holding Time Table

Matrix	Methods	Sample Container	Minimum Sample Size	Preservation	Dechlorination Agent	Holding Time[1]
Water: Total Sulfide	EPA 376.1 SM4500S2-F EPA 9034	250mL plastic	250mL	2N ZnAc/NaOH	None	7 days
Water: Acid Soluble	EPA 9030/9034	250mL plastic	6mL	2N ZnAc/NaOH	None	7 Days[2] 8 Hours[3]
Solid: Acid Soluble	EPA 9030/9034	4oz glass	1g	None	None	14 Days[2] 8 Hours[3]

[1]Unless noted, holding time is from collection to analysis
[2]From collection to distillation
[3]From distillation to analysis

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Attachment 3:
QC Summary

QC Item	Frequency	Criteria	Corrective Action
Batch Definition	Prepared/Analyzed together w/in 24-hr timeframe; not to exceed 20 field samples	Not Applicable	Not Applicable
Method Blank (MB)	One per batch	result <1/2 RL	Evaluate according to SOP SA-QA-17
Laboratory Control Sample (LCS)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Laboratory Control Sample Duplicate (LCSD)	One per batch, if insufficient sample provided for MS/MSD	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Low-Level Laboratory Control Sample (LLCS)	One per batch (Drinking Water only)	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Matrix Spike (MS)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Sample Duplicate (SD)	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Initial Demonstration of Capability (IDOC)	Initially, per analyst, per analyte/method/matrix combination	Within limits listed in the MLG	Refer to SOP SA-QA-06 Note: Unsupervised work must not begin until acceptable IDOC is obtained.
Continuing Demonstration of Capability (CDOC)	Annually, per analyst, per analyte/method combination	Within limits listed in the MLG	Refer to SOP SA-QA-06
Reporting Limit	Upon method/instrument set-up, per	Refer to SOP SA-QA-07	Refer to SOP SA-QA-07

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QC Item	Frequency	Criteria	Corrective Action
Verification (RLV)	analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for NELAC)		

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Attachment 4:
Instrument Maintenance and Troubleshooting

Instrument Labeling
Each instrument must be labeled with its name or ID (e.g., MSA, ICP-D, etc.). Additionally, non-operational instruments must be isolated from service or marked as being out of service. Each piece of equipment has an "Operational / Not Operational" sticker that is used for this purpose.

Maintenance Log
A maintenance log must be established for each piece of equipment used in the laboratory. All maintenance that is performed on the instrument must be recorded in the log including:

- analyst or technician performing the maintenance
- date the maintenance was performed
- detailed explanation of the reason for the maintenance
- resolution of the problem and return to control
- all service calls from instrument representatives

Preventive Maintenance
There are no items pertaining to the micro-distillation unit for this section.

Desiccator Maintenance

Upright Desiccators with Doors

The following checks must be performed daily:

- Desiccant is active
- Hygrometer is in the low humidity zone
- Door is making an air tight seal

The desiccator door must remain closed and seated whenever possible.

When the desiccant turns from blue to light purple, discard desiccant, in accordance with the TestAmerica Savannah Addendum to the EHSM, and refill pan with fresh desiccant.

Troubleshooting
There are no items for this section.

Contingency Plan
In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved TestAmerica location.

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18.0 Revision History

Summary of Changes from Previous Revision:

- Minor editorial, grammatical, and formatting changes made. Boilerplate text added.
- Revised procedure to include micro-distillation apparatus. Removed reference to and procedures for MIDI apparatus.
- Removed reference to dissolved sulfide. This procedure is no longer performed.
- Clarified reference to acid soluble
- Revised Safety section to include materials and concerns associated with micro-distillation procedure. Updated formaldehyde TWA.
- Updated SOP references to reflect current titles and document control numbers.
- Updated Lab Supplies section to reflect current procedures/equipment (included beakers and Parafilm).
- Updated Reagents and Standards section to reflect current practice.
- Added note that titration must be performed slowly around the pale yellow and blue to cleat determination. Section 10.3.14

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APPENDIX C

EXAMPLE CHAIN-OF-CUSTODY FORM

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