



QUALITY ASSURANCE PROJECT PLAN

PORTAGE CREEK AREA REMOVAL KALAMAZOO, MICHIGAN

Prepared for:

**U.S. Environmental Protection Agency
Region 5**

Prepared by:



**Environmental Quality
Management, Inc.**

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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

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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
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	dichlorobenzene
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
GI	glass
GPS	global positioning system
H ₂ SO ₄	sulfuric acid
HASP	Health and Safety Plan
HAZWOPER	Hazardous Waste Operations and Emergency

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
PAH	polynuclear aromatic hydrocarbons
PCB	polychlorinated biphenyls
PEL	permissible exposure limit
PI	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

ACRONYMS – CONTINUED

RBSLs	Rick Based Screening Levels
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

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

Angve Dragotta, Environmental Quality Management, Inc. (EQ) Emergency and Rapid
Response Services (ERRS) Contractor

Preparer's Name and Organizational Affiliation

1800 Carillon Blvd, Cincinnati, OH 45240, adragotta@eqm.com

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

03/29/13

Preparation Date (Month/Day/Year)

Investigative Organization's Project Manager:

Signature

Eric Bowman

3/29/13

Eric Bowman, EQ, ERRS Contractor, March 29, 2013

Printed Name/Organization/Date Printed

Investigative Organization's Project QA Officer:

Signature

Angve Dragotta

3/29/13

Angve Dragotta, EQM ERRS Contractor, March 29, 2013

Printed Name/Organization/Date

Lead Organization's Project Manager:

Signature

C. Thomas

3/29/13

Craig Thomas, U.S. EPA Region V, March 29, 2013

Printed Name/Organization/Date

Approval Signatures:

Signature

Ida Levin

4/02/13

Ida Levin, QAPP Reviewer, U.S. EPA Region V

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 (OSCs) Paul Ruesch, Andrew Maguire and Craig Thomas

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: _____

Worksheet #2 – continued

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	Crosswalk to Worksheet No. or Related Documents
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QAPP Worksheet #3 Distribution List

QAPP Recipients	Title	Organization	Telephone Number	E-mail Address	Document Control Number
Craig Thomas	OSC	U.S. EPA	312 886 5907	Thomas.craig@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 Site Response Manager (RM)	EQ	513-265-8875	ebowman@eqm.com	
Angye Dragotta	ERRS Sample Management Coordinator / Project QA Officer	EQ	513-742-7256	adragotta@eqm.com	
Mark Douglas	ERRS Site Sample Manager	EQ	513-309-3062	mdouglas@eqm.com	
Josh McKinney	Lab PM	Test America Laboratories, Inc.	937-294-6856	Josh.McKinney@testamericainc.com	
Tom Beamish	Lab PM	ALS Environmental	616-738-7318	Tom.Beamish@ALSGlobal.com	

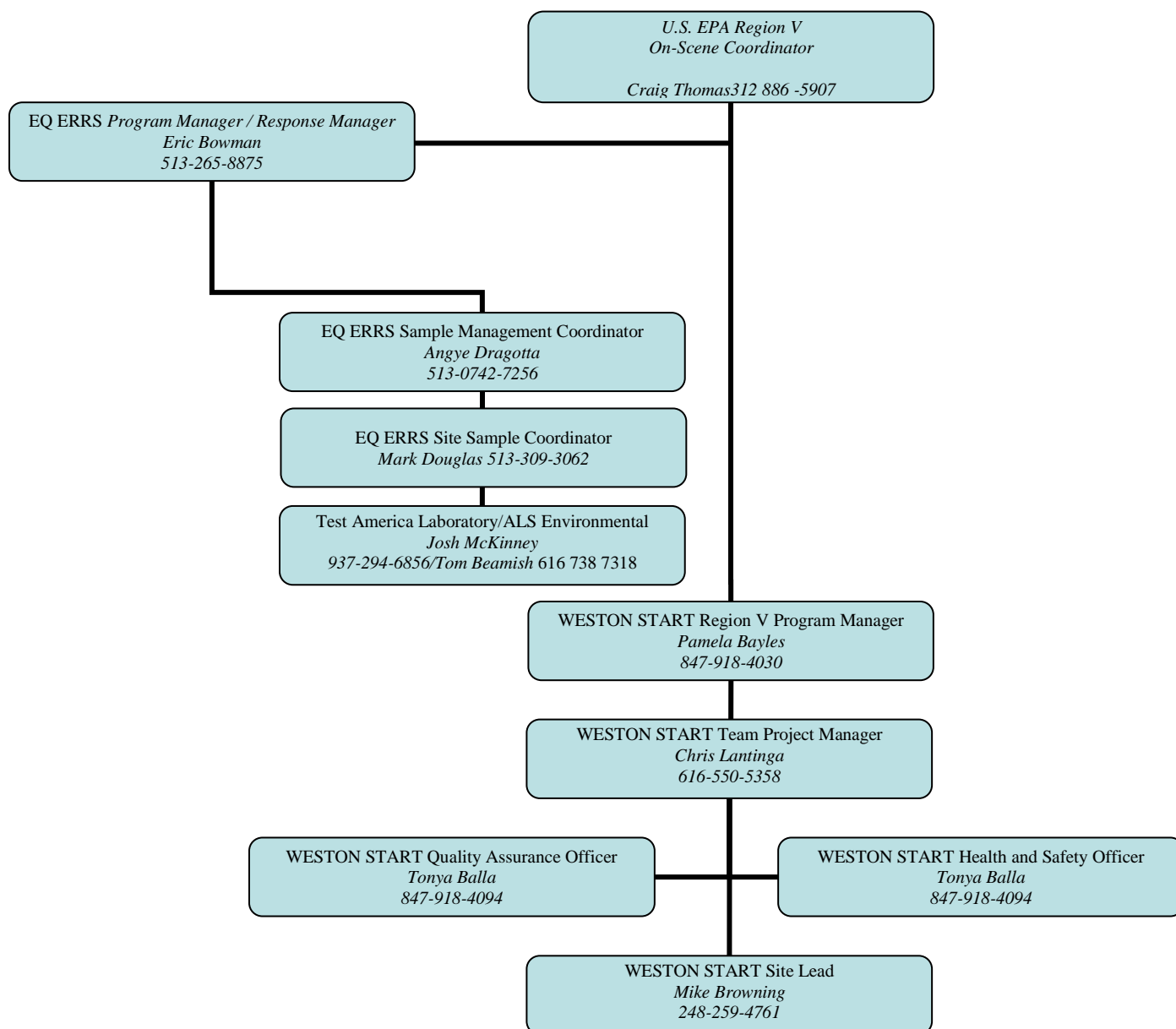
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QAPP Worksheet #4 Project Personnel Sign-Off Sheet

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Craig Thomas	U.S. EPA OSC	312-8- 886-5907		
Chris Lantinga	START PM	616-550-5358		
Tonya Balla	START Project QA Officer	847-918-4094		
Eric Bowman	ERRS Site RM	513-265-8875		
Angye Dragotta	ERRS Sample Management Coordinator / Project QA Officer	513- 742-7256		
Mark Douglas	ERRS Site Sample Manager	513-309-3062		

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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	Craig Thomas	312-886-5907	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 site 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	Eric Bowman	513-309-4703	The ERRS Site Response Manager will inform the ERRS Site 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	Angye Dragotta	513-742-7256	The ERRS Site Response Manager will inform the OSC, WESTON Site Leader and the ERRS Sample Management Coordinator of daily field progress while on site by email or phone. 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	Angye Dragotta / Tonya Balla	513-825-7500/ 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	Craig Thomas/ Eric Bowman/ Tonya Balla	312-886-5907/ 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	Angye Dragotta / Tonya Balla	513-825-7500 / 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	Craig Thomas	312- 886-5907	Approval of all QAPP amendments will be by the OSC prior to the changes being implemented.

QAPP Worksheet #7 Personnel Responsibilities and Qualifications Table

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Craig Thomas	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
Angye Dragotta / 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. Biology; over 14 years of experience / B.S. Environmental Sampling; over 18 years experience
Mark Douglas	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.	BS Biology, over 25 years experience
Josh McKinney	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. Zoology; 11 years of experience
Tom Beamish	Lab PM	ALS Environmental		B.S. Environmental Science, 30 years of experience

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/Certificates¹
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
John Wentz	Engineer	EQ	513-825-7500	jwentz@eqm.com	Project Engineer
Mike Arozarena	Engineer	EQ	513-825-7500	marozarena@eqm.com	Permitting Support
Jill Binzer	Scientist	EQ	513-825-7500	jbenzer@eqm.com	Permitting Support
Aziz Omara	Engineer	EQ	219-844-3500	aomara@eqengineers.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.

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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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.

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 an 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

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.

Worksheet #10 – continued

TABLE 10a. PRE-REMOVAL SEDIMENT SAMPLING

Removal Area	Grid	Depth of Samples	No. Cores in Grid	No. of anticipated samples per core
<i>Area 7</i>				
	SA7-4	24 in	2	2
<i>Area 6</i>				
	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
<i>Axtell Creek</i>				
	AXC-1	36 in	1	3
	AXC-3	24 in	1	2
<i>Area 5D</i>				
	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
<i>Areas 5C</i>				
	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
<i>Areas 5A</i>				
	SA5-A5	48in	1	4
	SA5-A6	48in	1	4
	SA5-A7	48in	1	4
<i>Area 3A</i>				
	SA3-A1	36 in	1	3
	SA3-A2	36 in	1	3
	SA3-A7	36 in	1	3
<i>Area 1A</i>				
	SA1-A9	36 in	1	3

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 exceedence	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, ALS Environmental and Test America Laboratories. The samples will be analyzed by Test America Laboratories, Inc. in North Canton, Ohio; Savannah, Georgia; and Phoenix, Arizona. The Phoenix facility will analyze the air samples, Savannah will analyze for herbicides and sulfide, and the North Canton Test America facility will analyze all other samples. Quick turn around time confirmation PCB samples will be analyzed by ALS at the Holland, Michigan facility.

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.

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
	wipe	confirm decontamination of equipment prior to removal from site	TBD	TBD	TBD	TBD	surface wipe
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

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Worksheet #11 – continued

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

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)
<ul style="list-style-type: none"> 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/ NC-WC-004 4500P /.8NC-WC-050608/ NC-GC-007, Rev. 5	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/ HN-GC-002-R06	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

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/ NC-GC-038	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

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/NC-OP-033 SW846 8260/ NC-MS-019, SW846 8270/ NC-MS-018 SW846 6010B/ NC-MT-012 SW846 7471B/ NC-MT-014 SW846 8081/ NC-GC-038 SW846 8015/ Herbicides SAV SW846 9012/NC-WC-032 SW846 9034/SOP Sulfide soil SAV SW846 1010/NC-WC-034 SW846 9045/NC-WC-010 SW846 9095/NC-WC-046	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

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/ NC-MS-019, SW846 8270/ NC-MS-018, SW846 6010/ NC-MT-012 SW846 8260/ NC-MT-002, SW846 7471B/ NC-MT-014, SW846 8081/ NC-GC-038, SW846 8082/ NC-GC-038 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

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/ NC-MS-019, SW846 8270/ NC-MS-018, NC-MT-012SW846 6010B/ NC-MT-012 SW846 6020/ NC-MT-002 SW846 7471B/ NC-MT-014 SW846 8081/ NC-GC-038, SW846 8082/ NC-GC-038, 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

Worksheet #12 – continued

QAPP Worksheet #12-7

Matrix	Air				
Analytical Group	PCB, PAH 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 NIOSH 5506/SOP PE-IHD-008 R.2	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

Worksheet #12 – continued

QAPP Worksheet #12-8

Matrix	Wipe (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 wipe sample per piece of equipment prior to leaving site	SW846 8082/ HN-GC-002-R06	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, 2. LCS 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

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. <i>Portage Creek Remediation: Volume and Mass Estimations</i> . 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

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, Test America-Savannah will process samples for herbicides and sulfide analysis and the Test America -North Canton, Ohio facility will prepare and process all other samples for analysis, with the exception of the quick turn confirmation sediment samples and PCB wipes. The quick turn PCB (sediment and wipe) samples will be analyzed by ALS in Holland, MI.

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

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Worksheet #14 – continued

Data Management Tasks:

Data will be evaluated against the applicable project action levels.

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. 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. 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. A compliance check of all data received will be performed by the ERRS or START chemist prior to utilizing in any report.

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	-	-	1.8	4
Total Phosphorus	7723-14-0	-	0.033	0.100
Total PCB	-	0.200 ug/L	0.073ug/L	0.1 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)	ALS MDL (mg/kg)	ALS RL (mg/kg)
PCB-1016	12674-11-2	*	0.03559	0.040
PCB-1221	11104-28-2	*	0.03559	0.040
PCB-1232	11141-16-5	*	0.03559	0.040
PCB-1242	53469-21-9	*	0.03559	0.040
PCB-1248	12672-29-6	*	0.03559	0.040
PCB-1254	11097-69-1	*	0.01116	0.040
PCB-1260	11096-82-5	*	0.01116	0.0400

*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	*	0.021	0.033
PCB-1221	11104-28-2	*	0.016	0.033
PCB-1232	11141-16-5	*	0.014	0.033
PCB-1242	53469-21-9	*	0.013	0.033
PCB-1248	12672-29-6	*	0.017	0.033
PCB-1254	11097-69-1	*	0.017	0.033
PCB-1260	11096-82-5	*	0.017	0.033

*Results will be used for information purposes only

UFP QAPP Worksheet #15-4

Matrix: Solid

Analytical Group: Waste Characterization TCLP (SW846 1311/*)

Concentration Level: High

Analyte	*Analytical Method	CAS Number	Project Action Limit (mg/L)	Test America MDL (mg/L)	Test America RL (mg/L)
Arsenic	SW846 6010B	7440-38-2	5.0	0.0032	0.5
Barium	SW846 6010B	7440-39-3	100.0	0.00067	10
Benzene	SW846 8260B	71-43-2	0.5	0.0065	0.025
Cadmium	SW846 6010B	7440-43-9	1.0	0.00066	0.1
Carbon Tetrachloride	SW846 8260B	56-23-5	0.5	0.0065	0.025
Chlorobenzene	SW846 8260B	108-90-7	100.0	0.0075	0.025
Chloroform	SW846 8260B	67-66-3	6.0	0.008	0.025
Chromium	SW846 6010B	7440-47-3	5.0	0.0022	0.5
o-Cresol	SW846 8270C	95-48-7	200.0	0.0008	0.004
m-Cresol ¹	SW846 8270C	108-39-4	200.0	0.00075	0.04
p-Cresol ¹	SW846 8270C	106-44-5	200.0	0.00075	0.04
1,4-Dichlorobenzene	SW846 8270C	106-446-7	7.5	0.00034	0.004
1,2-Dichloroethane	SW846 8260B	107-06-2	0.5	0.011	0.025
1,1-Dichloroethylene	SW846 8260B	75-35-4	0.7	0.0095	0.025
2,4-Dinitrotoluene	SW846 8270C	121-14-2	0.13	0.00027	0.02
Hexachlorobenzene	SW846 8270C	118-74-1	0.13	0.0001	0.02
Hexachlorobutadiene	SW846 8270C	87-68-3	0.5	0.00027	0.02
Hexachloroethane	SW846 8270C	67-72-1	3.0	0.0008	0.02
Lead	SW846 6010B	7439-92-1	5.0	0.0019	0.5
Mercury	SW846 7470A	7439-97-6	0.2	0.00012	0.002
Methyl ethyl ketone	SW846 8260B	78-93-3	200.0	0.0285	0.25
Nitrobenzene	SW846 8270C	98-95-3	2.0	0.00004	0.004
Pentachlorophenol	SW846 8270C	87-86-5	100.0	0.0024	0.04
Pyridine	SW846 8270C	110-86-1	5.0	0.00035	0.02
Selenium	SW846 6010B	7782-49-2	1.0	0.0041	0.25
Silver	SW846 6010B	7440-22-4	5.0	0.0022	0.5
Tetrachloroethylene	SW846 8260B	127-18-4	0.7	0.0145	0.025
Trichloroethylene	SW846 8260B	79-01-6	0.5	0.0085	0.025
2,4,5-Trichlorophenol	SW846 8270C	95-95-4	400.0	0.0003	0.02
2,4,6-Trichlorophenol	SW846 8270C	88-06-2	2.0	0.0008	0.02
Vinyl chloride	SW846 8260B	75-01-4	0.2	0.011	0.025

¹ Will be reported as 3,4-methylphenol

UFP QAPP Worksheet #15-5

Matrix: Solid

Analytical Group: Waste Characterization Wet Chem (SW846)

Concentration Level: High

Analyte	Analytical Method	CAS Number	Project Action Limit (mg/kg)	Test America MDL (mg/kg)	Test America RL (mg/kg)
Total Cyanide	SW846 9012	57-12-5	250	0.1	0.5
Reactive Sulfide	SW846 9034	18496-25-8	500	10	50
Flashpoint	SW846 1010 (mod)	-	60°C	-	32°C
pH	SW846 9045D	-	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 #15-6a

Matrix: Air

Analytical Group: Worker Exposure Assessment (PAH by NIOSH 5506)

Concentration Level: Low

Analyte	CAS Number	Project Action Limit (mg/m ³)	Test America RL (µg/sample)
Acenaphthylene	208-96-8		2
Anthracene	120-12-7		2.5
Benzantrhacene	56-55-3		0.25
Benzo(a)pyrene	50-32-8		0.25
Benzo(b)fluoranthene	205-99-2		0.50
Benzo (g,h,i)perylene	191-24-2		0.50
Benzo (k) fluoranthene	207-08-9		0.25
Chrysene	218-01-9		0.25
Dibenz (a,h)anthracene	53-70-3		0.50

Worksheet #15 – continued

Analyte	CAS Number	Project Action Limit (mg/m³)	Test America RL (µg/sample)
Fluoranthene	206-44-0		0.5
Fluorene	86-73-7		0.5
Indeno(1,2,3-c,d)pyrene	193-39-5		0.25
Naphthalene	91-20-3		1.0
Phenanthrene	85-01-8		0.25
Pyrene	129-00-0		0.25

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/m³)	Test America MDL (µg/sample)	Test America RL (µg/sample)
Particulates	-	15	38	100

UFP QAPP Worksheet #15-8

Matrix: Solid

Analytical Group: Pre- and Post-Construction Staging/Support Areas Metals (SW846)

Concentration Level: Medium

Analyte	Analytical Method	CAS Number	Project Action Limit* (mg/kg)	Test America MDL (mg/kg)	Test America RL (mg/kg)
Aluminum	SW846 6010B	7429-90-5		9.6	20
Antimony	SW846 6020A	7440-36-0		0.024	0.200
Arsenic	SW846 6010B	7440-38-2		0.3	1
Barium	SW846 6010B	7440-39-3		0.071	20
Beryllium	SW846 6010B	7440-41-7		0.043	0.5
Cadmium	SW846 6010B	7440-43-9		0.036	0.2
Calcium	SW846 6010B	7440-70-2		16	500
Chromium	SW846 6010B	7440-47-3		0.2	0.5
Cobalt	SW846 6010B	7440-48-4		0.16	5
Copper	SW846 6020A	7440-50-8		0.043	0.2
Iron	SW846 6010B	7439-89-6		4.9	10
Lead	SW846 6010B	7439-92-1		0.19	0.3
Magnesium	SW846 6010B	7439-95-4		5.1	500
Manganese	SW846 6020A	7439-96-5		0.047	0.5
Mercury	SW846 7471A	7439-97-6		0.015	0.1
Nickel	SW846 6010B	7440-02-0		0.27	4
Potassium	SW846 6010B	7440-09-7		6.2	500
Selenium	SW846 6010B	7782-49-2		0.45	0.5
Silver	SW846 6010B	7440-22-4		0.1	0.5
Sodium	SW846 6010B	7440-23-5		66	500
Thallium	SW846 6020A	7440-28-0		0.013	0.2
Vanadium	SW846 6010B	7440-62-2		0.12	5
Zinc	SW846 6010B	7440-66-6		1	2

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

Worksheet #15 – continued

UFP QAPP Worksheet #15-9

Matrix: Solid

Analytical Group: Pre- and Post-Construction Staging/Support Areas SVOC (SW846 8270)

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		3.3	6.67
Acenaphthylene	208-96-8		3.3	6.67
Acetophenone	98-86-2		9.2	100
2-Acetylaminofluorene	53-96-3		120	330
4-Aminobiphenyl	92-67-1		97	330
Aniline	62-53-3		80	330
Anthracene	120-12-7		3.3	6.67
Benzo (a) anthracene	56-55-3		3.3	6.67
Benzo (b) fluoranthene	205-99-2		3.3	6.67
Benzo (g,h,i) perylene	191-24-2		3.3	6.67
Benzo (k) fluoranthene	207-08-9		3.3	6.67
Benzo (a) pyrene	50-32-8		3.3	6.67
Benzidine	92-87-5		333	660
Benzyl alcohol	100-51-6		21	300
Bis(2-chloroethoxy)methane	111-91-1		22	100
Bis(2-chloroethyl)ether	111-44-4		2	100
Bis(2-chloroisopropyl) ether	108-60-1		9.5	100
Bis(2-ethylhexyl)phthalate	117-81-7		19	50
4-Bromophenyl phenyl ether	101-55-3		13	50
Butyl benzyl phthalate	85-68-7		10	50
Carbazole	86-74-8		27	50
4-Chloroaniline	106-47-8		17	150
Chlorobenzilate	510-15-6		3.4	330
4-Chloro-3-methylphenol	59-50-7		21	150
2-Chloronaphthalene	91-58-7		3.3	50
2-Chlorophenol	95-57-8		27	50
4-Chlorophenyl phenyl ether	7005-72-3		13	50
Chrysene	218-01-9		1.1	6.67
Diallate	2303-16-4		4.6	330
Dibenzofuran	132-64-9		3.3	50
1,2-Dichlorobenzene	95-50-1		9.7	50
1,3-Dichlorobenzene	541-73-1		11	50
1,4-Dichlorobenzene	106-46-7		20	50
Dibenz (a,h) anthracene	53-70-3		3.3	6.67
Di-n-butyl phthalate	84-74-2		15	50
3,3'-Dichlorobenzidine	91-94-1		18	100
2,4-Dichlorophenol	120-83-2		20	150
2,6-Dichlorophenol	87-65-0		4	200
Diethyl phthalate	84-66-2		16	50
7,12-Dimethylbenz (a) anthracene	57-97-6		120	330
Dimethoate	60-51-5		130	330
Dimethylaminoazobenzene	60-11-7		3.4	330

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)
3,3'-Dimethylbenzidine	119-93-7		63	330
2,4-Dimethylphenol	105-67-9		20	150
Dimethyl phthalate	131-11-3		17	50
1,3-Dinitrobenzene	99-65-0		120	330
4,6-Dinitro-2-methylphenol	534-52-1		80	150
2,4-Dinitrophenol	51-28-5		80	330
2,4-Dinitrotoluene	121-14-2		27	200
2,6-Dinitrotoluene	606-20-2		21	200
Di-n-octyl phthalate	117-84-0		27	50
Diphenylamine	122-39-4		21	100
Disulfoton	298-04-4		4.1	330
Ethyl methanesulfonate	62-50-0		4	330
Famphur	52-85-7		4.6	3300
Fluoranthene	206-44-0		3.3	6.67
Fluorene	86-73-7		3.3	6.67
Hexachlorobenzene	118-74-1		2.1	6.67
Hexachlorobutadiene	87-68-3		27	50
Hexachlorocyclopentadiene	77-47-4		27	330
Hexachloroethane	67-72-1		9	50
Hexachloropropene	1888-71-7		4.6	330
Indeno (1,2,3-cd) pyrene	193-39-5		3.3	6.67
Isodrin	465-73-6		6.4	330
Isophorone	78-59-1		13	50
Isosafrole	120-58-1		3.9	330
Kepone	143-50-0			
Methapyrilene	91-80-5		120	330
3-Methylcholanthrene	56-49-5		120	200
Methyl methanesulfonate	66-27-3		4.1	330
2-Methylnaphthalene	91-57-6		3.3	6.67
2-Methylphenol (o-Cresol)	95-48-7		80	200
3&4-Methylphenol (m&p Cresol)	-		20	400
Naphthalene	91-20-3		3.3	6.67
1,4-Naphthoquinone	130-15-4		110	330
1-Naphthylamine	134-32-7		3.6	330
2-Naphthylamine	91-59-8		3.7	200
2-Nitroaniline	88-74-4		9.1	200
3-Nitroaniline	99-09-2		16	200
4-Nitroaniline	100-01-6		17	150
Nitrobenzene	98-95-3		2.2	100
2-Nitrophenol	88-75-5		27	50
4-Nitrophenol	100-02-7		80	330
5-Nitro-o-toluidine	99-55-8		4.6	330
N-Nitrosodi-n-butylamine	924-16-3		7.5	100
N-Nitrosodiethylamine	55-18-5		4.3	100

3281-87PCA.1

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-Nitrosodimethylamine	62-75-9		16	100
N-Nitrosomethylethylamine	10595-95-6		5.2	100
N-Nitrosodiphenylamine	86-30-6		21	50
N-Nitrosodi-n-propylamine	621-64-7		27	50
N-Nitrosomorpholine	59-89-2		5.1	330
N-Nitrosopiperidine	100-75-4		110	330
N-Nitropyrrolidine	930-55-2		3.9	50
Parathion-methyl	298-00-0		130	330
Parathion	-		120	330
Pentachlorobenzene	608-93-5		5.4	100
Pentachlorophenol	87-86-5		80	150
Pentachloronitrobenzene	82-68-8		6	330
Phenacetin	62-44-2		6.7	330
Phenanthrene	85-01-8		3.3	6.67
Phenol	108-95-2		27	50
1,4-Phenylenediamine	106-50-3		61	660
Phorate	298-02-2		5.9	330
2-Picoline	109-06-8		4.9	330
Pronamide	23950-58-5		4.8	330
Pyrene	129-00-0		3.3	6.67
Pyridine	110-86-1		27	100
Safrole	94-59-7		4.3	330
Sulfotepp	3689-24-5		6.5	33
1,2,4,5-Tetrachlorobenzene	95-94-3		5.3	100
Thionazin	297-97-2		6.5	330
o-Toluidine	95-53-4		4.9	330
2,3,4,6-Tetrachlorophenol	58-90-2		110	1600
1,2,4-Trichlorobenzene	120-82-1		27	50
2,4,5-Trichlorophenol	95-95-4		25	150
2,4,6-Trichlorophenol	88-06-2		80	150
O,O,O-Triethyl phosphorothioate	126-68-1		5.5	330
1,3,5-Trinitrobenzene	99-35-4		100	1600

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

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		6.3	20
Acrolein	107-02-8		3.7	100
Acrylonitrile	107-13-1		3.7	100
Allyl chloride	107-05-1		0.89	10
Benzene	71-43-2		0.23	5
Bromodichloromethane	75-27-4		0.28	5
Bromoform	75-25-2		0.33	5
Bromomethane (Methyl bromide)	74-83-9		0.54	5
2-Butanone (MEK)	78-93-3		1.4	20
Carbon disulfide	75-15-0		0.44	5
Carbon tetrachloride	56-23-5		0.37	5
Chlorobenzene	108-90-7		0.33	5
Chloroethane	75-00-3		0.86	5
Chloroform	67-66-3		0.29	5
Chloromethane (Methyl chloride)	74-87-3		0.41	5
Chloroprene	126-99-8		0.37	5
Dibromochloromethane	124-48-1		0.55	5
1,2-Dibromo-3-chloropropane	96-12-8		1.3	10
1,2-Dibromoethane (EDB)	106-93-4		0.5	5
Dibromomethane	74-95-3		0.63	5
trans-1,4-Dichloro-2-butene	110-57-6		0.93	5
1,2-Dichlorobenzene	95-50-1		0.36	5
1,4-Dichlorobenzene	106-46-7		0.66	5
1,3-Dichlorobenzene	541-73-1		0.35	5
Dichlorodifluoromethane	75-71-8		0.5	5
1,1-Dichloroethane	75-34-3		0.36	5
1,2-Dichloroethane	107-06-2		0.34	5
trans-1,2-Dichloroethene	156-60-5		0.41	5
1,2-Dichloroethene (total)	540-59-0		0.77	10
1,1-Dichloroethene	75-35-4		0.52	5
1,2-Dichloropropane	78-87-5		0.69	5
cis-1,3-Dichloropropene	10061-01-5		0.34	5
1,3-Dichloropropene (total)	NA		0.42	10
trans-1,3-Dichloropropene	10061-02-6		0.54	5
Ethylbenzene	100-41-4		0.26	5
Hexachlorobutadiene	87-68-3		1.2	5
Ethyl methacrylate	97-63-2		0.41	5
2-Hexanone	591-78-6		0.63	20
Iodomethane	74-88-4		0.54	5
Methacrylonitrile	126-98-7		0.28	5
Methylene chloride	75-09-2		0.67	5
Methyl methacrylate	80-62-6		0.54	5

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		0.54	20
Propionitrile	107-12-0		2.8	20
Styrene	100-42-5		0.4	5
1,1,1,2-Tetrachloroethane	630-20-6		0.15	5
1,1,2,2-Tetrachloroethane	79-34-5		0.62	5
Tetrachloroethene	127-18-4		0.34	5
Toluene	108-88-3		0.52	5
1,2,4-Trichlorobenzene	120-82-1		0.27	5
1,1,1-Trichloroethane	71-55-6		0.65	5
1,1,2-Trichloroethane	79-00-5		0.56	5
Trichloroethene	79-01-6		0.39	5
Trichlorofluoromethane	75-69-4		0.42	5
1,2,3-Trichloropropane	96-18-4		0.34	5
Vinyl Acetate	108-05-4		0.9	5
Vinyl chloride	75-01-4		0.25	10
m,p-Xylene	1330-20-7		0.39	5
o-Xylene	95-47-6		1.2	10
Xylenes, total	1330-20-7		0.35	5

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

Worksheet #15 – continued

UFP QAPP Worksheet #15-11

Matrix: Rinseate - liquid

Analytical Group: Pre- and Post-Construction Staging/Support Areas VOCs (SW846 8260)

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		1.1	10
Acrolein	107-02-8		2.2	20
Acrylonitrile	107-13-1		2	20
Allyl chloride	107-05-1		0.35	2
Benzene	71-43-2		0.13	1
Bromodichloromethane	75-27-4		0.15	1
Bromoform	75-25-2		0.64	1
Bromomethane (Methyl bromide)	74-83-9		0.41	1
2-Butanone (MEK)	78-93-3		0.57	10
Carbon disulfide	75-15-0		0.13	1
Carbon tetrachloride	56-23-5		0.13	1
Chlorobenzene	108-90-7		0.15	1
Chloroethane	75-00-3		0.29	1
Chloroform	67-66-3		0.16	1
Chloromethane (Methyl chloride)	74-87-3		0.3	1
Chloroprene	126-99-8		0.29	2
Dibromochloromethane	124-48-1		0.18	1
1,2-Dibromo-3-chloropropane	96-12-8		0.67	2
1,2-Dibromoethane (EDB)	106-93-4		0.24	1
Dibromomethane	74-95-3		0.28	1
trans-1,4-Dichloro-2-butene	110-57-6		0.15	1
1,2-Dichlorobenzene	95-50-1		0.13	1
1,4-Dichlorobenzene	106-46-7		0.14	1
1,3-Dichlorobenzene	541-73-1		0.13	1
Dichlorodifluoromethane	75-71-8		0.31	1
1,1-Dichloroethane	75-34-3		0.15	1
1,2-Dichloroethane	107-06-2		0.22	1
trans-1,2-Dichloroethene	156-60-5		0.19	1
1,2-Dichloroethene (total)	540-59-0		0.34	2
1,1-Dichloroethene	75-35-4		0.19	1
1,2-Dichloropropane	78-87-5		0.18	1
cis-1,3-Dichloropropene	10061-01-5		0.14	1
1,3-Dichloropropene (total)	NA		0.22	2
trans-1,3-Dichloropropene	10061-02-6		0.19	1
Ethylbenzene	100-41-4		0.17	1
Hexachlorobutadiene	87-68-3		0.3	1
Ethyl methacrylate	97-63-2		0.14	1
2-Hexanone	591-78-6		0.41	10
Iodomethane	74-88-4		0.18	1
Methacrylonitrile	126-98-7		0.51	2
Methylene chloride	75-09-2		0.33	1
Methyl methacrylate	80-62-6		0.49	2
4-Methyl-2-pentanone (MIBK)	108-10-1		0.32	10

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)
Propionitrile	107-12-0		1.2	4
Styrene	100-42-5		0.11	1
1,1,1,2-Tetrachloroethane	630-20-6		0.23	1
1,1,2,2-Tetrachloroethane	79-34-5		0.18	1
Tetrachloroethene	127-18-4		0.29	1
Toluene	108-88-3		0.13	1
1,2,4-Trichlorobenzene	120-82-1		0.15	1
1,1,1-Trichloroethane	71-55-6		0.22	1
1,1,2-Trichloroethane	79-00-5		0.27	1
Trichloroethene	79-01-6		0.17	1
Trichlorofluoromethane	75-69-4		0.21	1
1,2,3-Trichloropropane	96-18-4		0.43	1
Vinyl Acetate	108-05-4		0.19	2
Vinyl chloride	75-01-4		0.22	1
m,p-Xylene	1330-20-7		0.24	2
o-Xylene			0.14	1
Xylenes, total	1330-20-7		0.28	2

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

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	Analytical Method	CAS Number	Project Action Limit* (mg/kg)	Test America MDL (mg/kg)	Test America RL (mg/kg)
Aldrin	SW846 8081	309-00-2		0.0012	0.0017
alpha-BHC		319-84-6		0.00073	0.0017
beta-BHC		319-85-7		0.0011	0.0017
gamma-BHC (Lindane)		58-89-9		0.00074	0.0017
delta-BHC		319-86-8		0.0012	0.0017
Chlordane		57-74-9		0.0035	0.017
alpha-Chlordane		5103-71-9		0.00094	0.0017
gamma-Chlordane		12789-03-6		0.00042	0.0017
Dieldrin		60-57-1		0.00047	0.0017
4,4'-DDD		72-54-8		0.00062	0.0017
4,4'-DDE		72-55-9		0.00039	0.0017
4,4'-DDT		50-29-3		0.0063	0.0017
Endosulfan I		959-98-8		0.00052	0.0017
Endosulfan II		33213-65-9		0.00082	0.0017
Endosulfan sulfate		1031-07-8		0.00087	0.0017
Endrin		72-20-8		0.0005	0.0017
Endrin aldehyde		7421-93-4		0.001	0.0017
Endrin ketone		53494-70-5		0.00063	0.0017
Heptachlor		76-44-8		0.0011	0.0017
Heptachlor epoxide		1024-57-3		0.0008	0.0017
Methoxychlor		72-43-5		0.0015	0.0033
Toxaphene		8001-35-2		0.019	0.067
PCB-1016	SW846 8082	12674-11-2		0.021	0.033
PCB-1221		11104-28-2		0.016	0.033
PCB-1232		11141-16-5		0.014	0.033
PCB-1242		53469-21-9		0.013	0.033
PCB-1248		12672-29-6		0.017	0.033
PCB-1254		11097-69-1		0.017	0.033
PCB-1260		11096-82-5		0.017	0.033

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

Worksheet #15 – continued

UFP QAPP Worksheet #15-13

Matrix: Solid

Analytical Group: Pre- and Post-Construction Staging/Support Areas Herbicides (SW846 8151)

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

Worksheet #15 – continued

UFP QAPP Worksheet #15-14

Matrix: Solid

Analytical Group: Borrow Source Metals (SW846)

Concentration Level: Medium

Analyte	Analytical Method	CAS Number	Project Action Limit (mg/kg)	Test America MDL (mg/kg)	Test America RL (mg/kg)
Aluminum	SW846 6010B	7429-90-5	50,000	9.6	20
Antimony	SW846 6020A	7440-36-0	180	0.024	0.200
Arsenic	SW846 6010B	7440-38-2	7.6	0.3	1
Barium	SW846 6010B	7440-39-3	37,000	0.071	20
Beryllium	SW846 6010B	7440-41-7	410	0.043	0.5
Cadmium	SW846 6010B	7440-43-9	550	0.036	0.2
Calcium	SW846 6010B	7440-70-2	-	16	500
Chromium	SW846 6010B	7440-47-3	790,000	0.2	0.5
Cobalt	SW846 6010B	7440-48-4	2,600	0.16	5
Copper	SW846 6020A	7440-50-8	20,000	0.043	0.2
Iron	SW846 6010B	7439-89-6	160,000	4.9	10
Lead	SW846 6010B	7439-92-1	400	0.19	0.3
Magnesium	SW846 6010B	7439-95-4	1,000,000	5.1	500
Manganese	SW846 6020A	7439-96-5	25,000	0.047	0.5
Mercury	SW846 7471A	7439-97-6	160	0.015	0.1
Nickel	SW846 6010B	7440-02-0	40,000	0.27	4
Potassium	SW846 6010B	7440-09-7	-	6.2	500
Selenium	SW846 6010B	7782-49-2	1,600	0.45	0.5
Silver	SW846 6010B	7440-22-4	2,500	0.1	0.5
Sodium	SW846 6010B	7440-23-5	1,000,000	66	500
Thallium	SW846 6020A	7440-28-0	35	0.013	0.2
Vanadium	SW846 6010B	7440-62-2	750	0.12	5
Zinc	SW846 6010B	7440-66-6	170,000	1	2

Worksheet #15 – continued

UFP QAPP Worksheet #15-15

Matrix: Liquid

Analytical Group: Borrow Source (Rinseate) Metals (SW846 6010B/7470A)

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		0.097	0.2
Antimony	7440-36-0		0.0018	0.01
Arsenic	7440-38-2		0.0032	0.01
Barium	7440-39-3		0.00067	0.2
Beryllium	7440-41-7		0.00046	0.005
Cadmium	7440-43-9		0.00066	0.002
Calcium	7440-70-2		0.13	5
Chromium	7440-47-3		0.0022	0.005
Cobalt	7440-48-4		0.0017	0.007
Copper	7440-50-8		0.0045	0.025
Iron	7439-89-6		0.081	0.1
Lead	7439-92-1		0.0019	0.003
Magnesium	7439-95-4		0.034	5
Manganese	7439-96-5		0.00041	0.015
Nickel	7440-02-0		0.0032	0.04
Potassium	7440-09-7		0.072	5
Selenium	7782-49-2		0.0041	0.005
Silver	7440-22-4		0.0022	0.005
Sodium	7440-23-5		0.59	5
Thallium	7440-28-0		0.0047	0.01
Vanadium	7440-62-2		0.00064	0.007
Zinc	7440-66-6		0.005	0.05
Mercury	7439-97-6		0.00012	0.0002

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

Worksheet #15 – continued

UFP QAPP Worksheet #15-16

Matrix: Solid

Analytical Group: Borrow Source SVOC (SW846 8270C)

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	3.3	6.67
Acenaphthylene	208-96-8	1.6E+6	3.3	6.67
Aniline	62-53-3	3.3E+5	80	330
Anthracene	120-12-7	2.3E+8	3.3	6.67
Benzo (a) anthracene	56-55-3	20,000	3.3	6.67
Benzo (b) fluoranthene	205-99-2	20,000	3.3	6.67
Benzo (g,h,i) perylene	191-24-2	2.5E+6	3.3	6.67
Benzo (k) fluoranthene	207-08-9	2.0E+5	3.3	6.67
Benzo (a) pyrene	50-32-8	2,000	3.3	6.67
Benzyl alcohol	100-51-6	5.8E+6	21	300
Bis(2-chloroethyl)ether	111-44-4	13,000	2	100
Bis(2-ethylhexyl) phthalate	117-81-7	2.8E+6	19	50
Butyl benzyl phthalate	85-68-7	3.1E+5	10	50
Carbazole	86-74-8	5.3E+5	27	50
4-Chloro-3-methylphenol	59-50-7	4.5E+6	21	150
2-Chloronaphthalene	91-58-7	5.6E+7	3.3	50
2-Chlorophenol	95-57-8	1.4E+6	27	50
Chrysene	218-01-9	2.0E+6	1.1	6.67
Dibenzofuran	132-64-9	-	3.3	50
Dibenz(a,h)anthracene	53-70-3	2,000	3.3	6.67
1,2-Dichlorobenzene	95-50-1	2.1E+5	9.7	50
1,3-Dichlorobenzene	541-73-1	1.7E+5	11	50
1,4-Dichlorobenzene	106-46-7	4.0E+5	20	50
Di-n-butyl phthalate	84-74-2	-	15	50
3,3'-Dichlorobenzidine	91-94-1	6,600	18	100
2,4-Dichlorophenol	120-83-2	6.6E+5	20	150
Diethyl phthalate	84-66-2	7.4E+5	16	50
2,4-Dimethylphenol	105-67-9	1.1E+7	20	150
Fluoranthene	206-44-0	4.6E+7	3.3	6.67
Dimethyl phthalate	131-11-3	-	16	50
Fluorene	86-73-7	2.7E+7	3.3	6.67
Hexachlorobenzene	118-74-1	8,900	2.1	6.67
Hexachlorobutadiene	87-68-3	1.0E+5	27	50
Hexachlorocyclopentadiene	77-47-4	7.2E+5	27	330
Hexachloroethane	67-72-1	2.3E+5	9	50
Indeno (1,2,3-cd) pyrene	193-39-5	20,000	3.3	6.67
Isophorone	78-59-1	2.4E+6	13	50
2-Methylnaphthalene	91-57-6	8.1E+6	3.3	6.67
Naphthalene	91-20-3	1.6E+7	3.3	6.67
Nitrobenzene	98-95-3	1.0E+5	2.2	100
2-Nitrophenol	88-75-5	6.3E+5	27	50
N-Nitrosodiphenylamine	86-30-6	1.7E+6	21	50

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)
N-Nitrosodi-n-propylamine	621-64-7	1,200	27	50
Pentachlorophenol	87-86-5	90,000	80	150
Phenanthrene	85-01-8	1.6E+6	3.3	6.67
Phenol	108-95-2	1.2E+7	27	50
Pyrene	129-00-0	2.9E+7	3.3	6.67
Pyridine	110-86-1	37,000	27	100
1,2,4-Trichlorobenzene	120-82-1	-	27	50
2,4,5-Trichlorophenol	95-95-4	2.3E+7	25	150
2,4,6-Trichlorophenol	88-06-2	7.1E+5	80	150

3281-87PCA.1

Worksheet #15 – continued

UFP 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		0.1	0.2
Acenaphthylene	208-96-8		0.1	0.2
Aniline	62-53-3		2.4	5
Anthracene	120-12-7		0.1	0.2
Benzo (a) anthracene	56-55-3		0.1	0.2
Benzo (b) fluoranthene	205-99-2		0.1	0.2
Benzo (g,h,i) perylene	191-24-2		0.1	0.2
Benzo (k) fluoranthene	207-08-9		0.1	0.2
Benzo (a) pyrene	50-32-8		0.1	0.2
Benzyl alcohol	100-51-6		0.38	5
Bis(2-chloroethyl)ether	111-44-4		0.1	1
Bis(2-ethylhexyl) phthalate	117-81-7		0.8	2
Butyl benzyl phthalate	85-68-7		0.8	1
Carbazole	86-74-8		0.28	1
4-Chloro-3-methylphenol	59-50-7		0.8	2
2-Chloronaphthalene	91-58-7		0.1	1
2-Chlorophenol	95-57-8		0.29	1
Chrysene	218-01-9		0.1	0.2
Dibenzofuran	132-64-9		0.1	1
Dibenz(a,h)anthracene	53-70-3		0.1	0.2
1,2-Dichlorobenzene	95-50-1		0.29	1
1,3-Dichlorobenzene	541-73-1		0.8	1
1,4-Dichlorobenzene	106-46-7		0.34	1
Di-n-butyl phthalate	84-74-2		0.67	1
3,3'-Dichlorobenzidine	91-94-1		0.37	5
2,4-Dichlorophenol	120-83-2		0.8	2
Diethyl phthalate	84-66-2		0.6	1
2,4-Dimethylphenol	105-67-9		0.8	2
Dimethyl phthalate			0.29	1
2,4-Dinitrotoluene	121-14-2		0.27	5
Fluoranthene	206-44-0		0.1	0.2
Fluorene	86-73-7		0.1	0.2
Hexachlorobenzene	118-74-1		0.1	0.2
Hexachlorobutadiene	87-68-3		0.27	1
Hexachlorocyclopentadiene	77-47-4		0.8	10
Hexachloroethane	67-72-1		0.8	1
Indeno (1,2,3-cd) pyrene	193-39-5		0.1	0.2
Isophorone	78-59-1		0.27	1
2-Methylnaphthalene	91-57-6		0.1	0.2
Naphthalene	91-20-3		0.1	0.2
Nitrobenzene	98-95-3		0.04	1
2-Nitrophenol	88-75-5		0.28	2
N-Nitrosodiphenylamine	86-30-6		0.31	1

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		0.8	1
Pentachlorophenol	87-86-5		2.4	5
Phenanthrene	85-01-8		0.1	0.2
Phenol	108-95-2		0.6	1
Pyrene	129-00-0		0.1	0.2
Pyridine	110-86-1		0.35	1
1,2,4-Trichlorobenzene	120-82-1		0.28	1
2,4,5-Trichlorophenol	95-95-4		0.3	5
2,4,6-Trichlorophenol	88-06-2		0.8	5

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

Worksheet #15 – continued

UFP QAPP Worksheet #15-18

Matrix: Solid

Analytical Group: Borrow Source (solid) VOCs (SW846 8260)

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	6.3	20
Acrolein	107-02-8	3.6E+6	3.7	100
Acrylonitrile	107-13-1	16,000	3.7	100
Allyl chloride	107-05-1	-	0.89	10
Benzene	71-43-2	1.8E+5	0.23	5
Bromobenzene	108-86-1	5.4E+5	0.33	5
Bromochloromethane	74-97-5	-	0.71	5
Bromodichloromethane	75-27-4	1.1E+5	0.28	5
Bromoform	75-25-2	8.2E+5	0.33	5
Bromomethane (Methyl bromide)	74-83-9	3.2E+5	0.54	5
2-Butanone (MEK)	78-93-3	2.7E+7	1.4	20
tert-Butylbenzene	98-06-6	2.5E+6	0.29	5
sec-Butylbenzene	135-98-8	2.5E+6	0.18	5
n-Butylbenzene	104-51-8	2.5E+6	0.23	5
Carbon disulfide	75-15-0	2.8E+5	0.44	5
Carbon tetrachloride	56-23-5	96,000	0.37	5
Chlorobenzene	108-90-7	2.6E+5	0.33	5
Chloroethane	75-00-3	9.5E+5	0.86	5
2-Chloroethylvinyl ether	110-75-8	-	1.4	50
Chloroform	67-66-3	1.2E+6	0.29	5
Chloromethane (Methyl chloride)	74-87-3	1.1E+6	0.41	5
Chloroprene	126-99-8	-	0.37	5
4-Chlorotoluene	106-43-4	-	0.41	5
2-Chlorotoluene	95-49-8	5.0E+5	0.4	5
Cyclohexane	110-82-7	2.2E+8	0.33	10
Dibromochloromethane	124-48-1	1.1E+5	0.55	5
1,2-Dibromo-3-chloropropane	96-12-8	-	1.3	10
1,2-Dibromoethane (EDB)	106-93-4	-	0.5	5
Dibromomethane	74-95-3	2.0E+6	0.63	5
trans-1,4-Dichloro-2-butene	110-57-6	-	0.93	5
1,2-Dichlorobenzene	95-50-1	2.1E+5	0.36	5
1,4-Dichlorobenzene	106-46-7	4.0E+5	0.66	5
1,3-Dichlorobenzene	541-73-1	1.7E+5	0.35	5
Dichlorodifluoromethane	75-71-8	1.0E+6	0.5	5
1,1-Dichloroethane	75-34-3	8.9E+5	0.36	5
1,2-Dichloroethane	107-06-2	91,000	0.34	5
cis-1,2-Dichloroethene	156-59-2	6.4E+5	0.36	5
trans-1,2-Dichloroethene	156-60-5	1.4E+6	0.41	5
1,2-Dichloroethene (total)	540-59-0	-	0.77	10
1,1-Dichloroethene	75-35-4	2.0E+5	0.52	5
1,3-Dichloropropane	142-28-9	-	0.34	5
2,2-Dichloropropane	594-20-7	-	0.94	5
1,2-Dichloropropane	78-87-5	1.4E+5	0.69	5

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)
1,1-Dichloropropene	563-58-6	-		
cis-1,3-Dichloropropene	10061-01-5	-	0.34	5
1,3-Dichloropropene (total)	NA	-	0.42	10
trans-1,3-Dichloropropene	10061-02-6	-	0.54	5
Diethyl ether	60-29-7	7.4E+6	0.61	5
Ethyl acetate	141-78-6	7.5E+6	0.8	10
Ethylbenzene	100-41-4	1.4E+5	0.26	5
Ethyl methacrylate	97-63-2	-	0.41	5
Hexachlorobutadiene	87-68-3	1.0E+5	1.2	5
n-Hexane	110-54-3	44,000	1.2	5
2-Hexanone	591-78-6	2.5E+6	0.63	20
Iodomethane	74-88-4	-	0.54	5
Isopropylbenzene (Cumene)	98-82-8	3.9E+5	0.16	5
p-Isopropyltoluene	99-87-6	-	0.21	5
Methacrylonitrile	126-98-7	-	0.28	5
Methyl tert-butyl ether	1634-04-4	1.5E+6	0.43	20
Methylene chloride	75-09-2	1.3E+6	0.67	5
Methyl methacrylate	80-62-6	-	0.54	5
2-Methylnaphthalene	91-57-6	8.1E+6	3.4	10
4-Methyl-2-pentanone (MIBK)	108-10-1	2.7E+6	0.54	20
Naphthalene	91-20-3	1.6E+7	0.19	5
2-Nitropropane	79-46-9	-	2.8	10
Propionitrile	107-12-0	-	2.8	20
n-Propylbenzene	103-65-1	2.5E+6	0.4	5
Styrene	100-42-5	4.0E+5	0.15	5
1,1,1,2-Tetrachloroethane	630-20-6	4.4E+5	0.62	5
1,1,2,2-Tetrachloroethane	79-34-5	53,000	0.34	5
Tetrachloroethene	127-18-4	88,000	0.52	5
Toluene	108-88-3	2.5E+5	0.27	5
1,2,3-Trichlorobenzene	87-61-6	-	0.38	5
1,2,4-Trichlorobenzene	120-82-1	9.9E+5	0.65	5
1,1,1-Trichloroethane	71-55-6	4.6E+5	0.56	5
1,1,2-Trichloroethane	79-00-5	1.8E+5	0.39	5
Trichloroethene	79-01-6	5.0E+5	0.42	5
Trichlorofluoromethane	75-69-4	5.6E+5	0.34	5
1,2,3-Trichloropropane	96-18-4	8.3E+5	0.9	5
1,1,2-Trichlorotrifluoroethane	76-13-1	-	1.3	5
1,2,4-Trimethylbenzene	95-63-6	1.1E+5	0.65	5
1,3,5-Trimethylbenzene	108-67-8	94,000	0.25	5
Vinyl Acetate	108-05-4	2.4E+6	0.25	10
Vinyl chloride	75-01-4	3,8000	0.39	5
m,p-Xylene	1330-20-7	-	1.2	10
o-Xylene	95-47-6	-	0.35	5
Xylenes, total	1330-20-7	1.5E+8	0.67	10

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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		1.1	10
Acrolein	107-02-8		2.2	20
Acrylonitrile	107-13-1		2	20
Allyl chloride	107-05-1		0.35	2
Benzene	71-43-2		0.13	1
Bromobenzene	108-86-1		0.13	1
Bromochloromethane	74-97-5		0.29	1
Bromodichloromethane	75-27-4		0.15	1
Bromoform	75-25-2		0.64	1
Bromomethane (Methyl bromide)	74-83-9		0.41	1
2-Butanone (MEK)	78-93-3		0.57	10
tert-Butylbenzene	98-06-6		0.13	1
sec-Butylbenzene	135-98-8		0.13	1
n-Butylbenzene	104-51-8		0.12	1
Carbon disulfide	75-15-0		0.13	1
Carbon tetrachloride	56-23-5		0.13	1
Chlorobenzene	108-90-7		0.15	1
Chloroethane	75-00-3		0.29	1
2-Chloroethylvinyl ether	110-75-8		0.99	10
Chloroform	67-66-3		0.16	1
Chloromethane (Methyl chloride)	74-87-3		0.3	1
Chloroprene	126-99-8		0.29	2
4-Chlorotoluene	106-43-4		0.18	1
2-Chlorotoluene	95-49-8		0.11	1
Cyclohexane	110-82-7		0.12	1
Dibromochloromethane	124-48-1		0.18	1
1,2-Dibromo-3-chloropropane	96-12-8		0.67	2
1,2-Dibromoethane (EDB)	106-93-4		0.24	1
Dibromomethane	74-95-3		0.28	1
trans-1,4-Dichloro-2-butene	110-57-6		0.15	1
1,2-Dichlorobenzene	95-50-1		0.13	1
1,4-Dichlorobenzene	106-46-7		0.14	1
1,3-Dichlorobenzene	541-73-1		0.13	1
Dichlorodifluoromethane	75-71-8		0.31	1
1,1-Dichloroethane	75-34-3		0.15	1
1,2-Dichloroethane	107-06-2		0.22	1
cis-1,2-Dichloroethene	156-59-2		0.17	1
trans-1,2-Dichloroethene	156-60-5		0.19	1
1,2-Dichloroethene (total)	540-59-0		0.34	2
1,1-Dichloroethene	75-35-4		0.19	1
1,3-Dichloropropane	142-28-9		0.16	1
2,2-Dichloropropane	594-20-7		0.13	1
1,2-Dichloropropane	78-87-5		0.18	1
1,1-Dichloropropene	563-58-6		0.13	1

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		0.14	1
1,3-Dichloropropene (total)	NA		0.22	2
trans-1,3-Dichloropropene	10061-02-6		0.19	1
Diethyl ether	60-29-7		0.31	2
Ethyl acetate	141-78-6		0.5	4
Ethylbenzene	100-41-4		0.17	1
Ethyl methacrylate	97-63-2		0.14	1
Hexachlorobutadiene	87-68-3		0.3	1
n-Hexane	110-54-3		0.26	1
2-Hexanone	591-78-6		0.41	10
Iodomethane	74-88-4		0.18	1
Isopropylbenzene (Cumene)	98-82-8		0.13	1
p-Isopropyltoluene	99-87-6		0.12	1
Methacrylonitrile	126-98-7		0.51	2
Methyl tert-butyl ether	1634-04-4		0.17	5
Methylene chloride	75-09-2		0.33	1
Methyl methacrylate	80-62-6		0.49	2
2-Methylnaphthalene	91-57-6		0.47	5
4-Methyl-2-pentanone (MIBK)	108-10-1		0.32	10
Naphthalene	91-20-3		0.24	1
2-Nitropropane	79-46-9		0.7	2
Propionitrile	107-12-0		1.2	4
n-Propylbenzene	103-65-1		0.14	1
Styrene	100-42-5		0.11	1
1,1,1,2-Tetrachloroethane	630-20-6		0.23	1
1,1,2,2-Tetrachloroethane	79-34-5		0.18	1
Tetrachloroethene	127-18-4		0.29	1
Toluene	108-88-3		0.13	1
1,2,3-Trichlorobenzene	87-61-6		0.17	1
1,2,4-Trichlorobenzene	120-82-1		0.15	1
1,1,1-Trichloroethane	71-55-6		0.22	1
1,1,2-Trichloroethane	79-00-5		0.27	1
Trichloroethene	79-01-6		0.17	1
Trichlorofluoromethane	75-69-4		0.21	1
1,2,3-Trichloropropane	96-18-4		0.43	1
1,1,2-Trichlorotrifluoroethane	76-13-1			
1,2,4-Trimethylbenzene	95-63-6		0.12	1
1,3,5-Trimethylbenzene	108-67-8		0.096	1
Vinyl Acetate	108-05-4		0.19	2
Vinyl chloride	75-01-4		0.22	1
m,p-Xylene	1330-20-7		0.24	2
o-Xylene	95-47-6		0.14	1
Xylenes, total	1330-20-7		0.28	2

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

Worksheet #15 – continued

UFP QAPP Worksheet #15-20

Matrix: Solid

Analytical Group: Borrow Source Pesticides/PCBs (SW846)

Concentration Level: Medium

Analyte	Analytical Method	CAS Number	Project Action Limit (ug/kg)	Test America MDL (ug/kg)	Test America RL (ug/kg)
Aldrin	SW846 8081	309-00-2	1,000	0.0012	0.0017
alpha-BHC		319-84-6	-	0.00073	0.0017
beta-BHC		319-85-7	-	0.0011	0.0017
gamma-BHC (Lindane)		58-89-9	8,300	0.00074	0.0017
delta-BHC		319-86-8	-	0.0012	0.0017
Chlordane		57-74-9	31,000	0.0035	0.017
alpha-Chlordane		5103-71-9	-	0.00094	0.0017
gamma-Chlordane		12789-03-6	-	0.00042	0.0017
Dieldrin		60-57-1	1,00	0.00047	0.0017
4,4'-DDD		72-54-8	95,000	0.00062	0.0017
4,4'-DDE		72-55-9	45,000	0.00039	0.0017
4,4'-DDT		50-29-3	57,000	0.0063	0.0017
Endosulfan I		959-98-8	-	0.00052	0.0017
Endosulfan II		33213-65-9	-	0.00082	0.0017
Endosulfan sulfate		1031-07-8	-	0.00087	0.0017
Endrin		72-20-8	65,000	0.0005	0.0017
Endrin aldehyde		7421-93-4	-	0.001	0.0017
Endrin ketone		53494-70-5	-	0.00063	0.0017
Heptachlor		76-44-8	5,000	0.0011	0.0017
Heptachlor epoxide		1024-57-3	3,100	0.0008	0.0017
Methoxychlor		72-43-5	1.9E+6	0.0015	0.0033
Toxaphene		8001-35-2	20,000	0.019	0.067
PCB-1016	SW846 8082	12674-11-2		0.021	0.033
PCB-1221		11104-28-2		0.016	0.033
PCB-1232		11141-16-5		0.014	0.033
PCB-1242		53469-21-9		0.013	0.033
PCB-1248		12672-29-6		0.017	0.033
PCB-1254		11097-69-1		0.017	0.033
PCB-1260		11096-82-5		0.017	0.033

Worksheet #15 – continued

UFP QAPP Worksheet #15-21

Matrix: Liquid

Analytical Group: Borrow Source (Rinseate) Pesticides/PCBs (SW846)

Concentration Level: Medium

Analyte	Analytical Method	CAS Number	Project Action Limit* (ug/L)	Test America MDL (ug/L)	Test America RL (ug/L)
Aldrin	SW846 8081	309-00-2		0.0096	0.05
alpha-BHC		319-84-6		0.007	0.05
beta-BHC		319-85-7		0.0084	0.05
gamma-BHC (Lindane)		58-89-9		0.0064	0.05
delta-BHC		319-86-8		0.0087	0.05
Chlordane		57-74-9		0.033	0.5
alpha-Chlordane		5103-71-9		0.014	0.05
gamma-Chlordane		12789-03-6		0.012	0.05
Dieldrin		60-57-1		0.0075	0.05
4,4'-DDD		72-54-8		0.0096	0.05
4,4'-DDE		72-55-9		0.0097	0.05
4,4'-DDT		50-29-3		0.016	0.05
Endosulfan I		959-98-8		0.013	0.05
Endosulfan II		33213-65-9		0.012	0.05
Endosulfan sulfate		1031-07-8		0.011	0.05
Endrin		72-20-8		0.011	0.05
Endrin aldehyde		7421-93-4		0.011	0.05
Endrin ketone		53494-70-5		0.0078	0.05
Heptachlor		76-44-8		0.008	0.05
Heptachlor epoxide		1024-57-3		0.0071	0.05
Methoxychlor		72-43-5		0.032	0.05
Toxaphene		8001-35-2		0.32	2
PCB-1016	SW846 8082	12674-11-2		0.17	0.5
PCB-1221		11104-28-2		0.13	0.5
PCB-1232		11141-16-5		0.16	0.5
PCB-1242		53469-21-9		0.22	0.5
PCB-1248		12672-29-6		0.1	0.5
PCB-1254		11097-69-1		0.16	0.5
PCB-1260		11096-82-5		0.17	0.5

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

Worksheet #15 – continued

UFP QAPP Worksheet #15-22

Matrix: Solid

Analytical Group: Borrow Source Herbicides (SW846 8151)

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

Worksheet #15 – continued

UFP QAPP Worksheet #15-23

Matrix: Liquid

Analytical Group: Borrow Source (Rinseate) Herbicides (SW846 8151)

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.

UFP QAPP Worksheet #15-24

Matrix: Wipe

Analytical Group: PCBs (SW846)

Concentration Level: Low

Analyte	CAS Number	Project Action Limit (mg/wipe)	ALS RL (mg/wipe)
PCB-1016	12674-11-2	-	0.0025
PCB-1221	11104-28-2	-	0.0025
PCB-1232	11141-16-5	-	0.0025
PCB-1242	53469-21-9	-	0.0025
PCB-1248	12672-29-6	-	0.0025
PCB-1254	11097-69-1	-	0.0025
PCB-1260	11096-82-5	-	0.0025

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.
- Wipe samples will be collected annually on all equipment that leaves the site. Sample to be collected from a 100cm² area.

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.

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

Sampling Location/ ID Number¹	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 Number¹	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
Field Equipment/ Equipment type MM/DD/YYYY	wipe	N/A	PCB	Low	TBD	SP-Othr-3	To ensure equipment leaving the work area is free of contamination
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

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

Notes:

1. ID – identification, SD – sediment, WC – waste characterization, SO – soil/solid, SW – surface water, AR – air, WW – waste water, BS – borrow source, W-wipe
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

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Worksheet #18 – continued

3. INF – influent, MID – between GAC, EFF – effluent
4. All dates are recorded as MMDDYY

QAPP Worksheet #19 Analytical SOP Requirements Table

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/ SOP Reference¹	Containers (number, size, and type)	Preservation Requirements	Maximum Holding Time (preparation/analysis)
Sediment /Soil	PCBs	Low/Med	SW846 8082/ NC-GC-038	1 8-oz glass jar	4°C	14 days for extraction, 40 days for analysis
Sediment	TCLP VOCs	High	SW1311/8260 NC-OP-033NC-MS-019	4-oz GI WM	4°C	14 days for TCLP extraction, 14 days for analysis
Sediment	TCLP SVOCs	High	SW1311/8270/ NC-OP-033NC-MS-018	8-oz GI WM ²	4°C	14 days for TCLP extraction, 7 days for preparative extraction, 40 days for analysis
Sediment	TCLP Pesticides	High	SW1311/8081/ NC-OP-033NC-GC-038	8-oz GI WM ²	4°C	14 days for TCLP extraction, 7 days for preparative extraction, 40 days for analysis
Sediment	TCLP Herbicides	High	SW1311/8151/ NC-OP-033/SOP Herbicides SAV	8-oz GI 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/ NC-OP-033/NC-MT-012 NC-MT-002 and NC-MT-014	8-oz GI 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/ NC-GC-038	4 oz, GI ²	4°C	14 days for analysis
Sediment	Total Cyanide	High	SW9012/NC-WC-032	4 oz, GI ²	4°C	14 days for analysis
Sediment	Total Sulfide	High	SW9034/SOP Sulfide SAV	4 oz, GI ²	4°C	7 days for analysis
Sediment	Flashpoint	High	SW1010/NC-WC-034	4 oz, GI ²	4°C	None
Sediment	pH	High	SW9045/NC-WC-010	4 oz, GI ²	4°C	Immediately
Solids (soil, sand, rock)	TCL VOCs	Low	SW8260/ NC-MS-019	4-oz GI WM	4°C	14 days for analysis
Solids (soil, sand, rock)	TCL SVOCs	Low	SW8270/ NC-MS-018	8-oz GI WM ³	4°C	14 days for extraction, 40 days for analysis
Solids (soil, sand, rock)	TCL Pesticides	Low	SW8081/NC-GC-038 NC-GC-038	8-oz GI 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 GI WM ³	4°C	14 days for extraction, 40 days for analysis
Solids (soil, sand, rock)	TAL Metals	Low	SW6010 or 6020 & 7471B/ NC-MT-002 NC-MT-014 and NC-MT-012,	8-oz GI WM ³	4°C	28 days for Hg and 6 months for all other metals
Solids (soil, sand, rock)	PCBs	Low	SW846 8082/ NC-GC-038	4-oz GI WM ³	4°C	14 days for analysis

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Worksheet #19 – continued

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/ SOP Reference¹	Containers (number, size, and type)	Preservation Requirements	Maximum Holding Time (preparation/analysis)
Wipe	PCBs	Low	SW8082/ HN-GC-002	4-oz Gl WM ⁸	Methanol, 4°C	14 days
Water ⁴	PCBs	Low	E608/ NC-GC-007	1 L Gl Amber	4°C	7 days for extraction, 40 days for analysis
Water ⁴	TSS	Low	SM2540D/NC-WC-004	500 ml, Plastic	4°C	7 days for analysis
Water ⁴	Phosphorus	Low	SM4500P/NC-WC-050	250 ml, Plastic	H ₂ SO ₄ , 4°C	28 days for analysis
Air	PCBs	Low	NIOSH 5503/ PE-IHD-015	filter, sorbet tube ⁵	4°C	2 months
Air	Total Particulates	Low	NIOSH 0500/ PE-IHD-002	PVC ⁶	None	None
Air	PAH	Low	NIOSH 5506/PE-IHD-008	filter, sorbent tube ⁷	0°C, protect from light	unknown

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 glass (GL), wide mouth (WM) 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 + florisol, 100 mg/50 mg)
6. 37-mm, 5-µm PVC filter
7. 37-mm, 2-µm, PTFE filter + washed XAD-2 sorbent tube, 100mg/50 mg
8. Gauze wipe

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QAPP Worksheet #20 Field Quality Control Sample Summary Table

Matrix	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference¹	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	NC-GC-038NC-GC-038	113	Once	12	NA	0	0	0	125
Sediment	Waste Characterization	High	DT-ORG-003.2, NC-MS-019, NC-MS-018, NC-MT-012.0, NC-MT-014, NC-GC-038, DOP Herbicides SAV, NC-WC-032, SOP Sulfide soil SAVNC-WC-034,NC WC-060, NC-WC-010, NC-WC-046	18-36	Once	0	0	0	0	0	TBD
Surface Soil	PCBs	Low	NC-GC-038NC-GC-038	12-20	Once	1/10	NA	0	0	0	14-22
Borrow Source ²	VOCs, SVOCs, Pesticides/PCBs, Herbicides, Metals	Low	NC-MS-019, NC-MS-018, NC-MT-012.0, NC-MT-002 NC-MT-014, NC-GC-038, , 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	NC-MS-019, NC-MS-018, NC-MT-012.0, NC-MT-002 NC-MT-014, NC-GC-038NC-GC-038, , SOP Herbicides SAV	TBD	2 times (pre & post construction)	1/10	1/20	0	0	0	TBD
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	NC-WC-004, NC-GC-007	TBD	Once per week during removal activities	1/10	0	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	Phosphorus	Low	NC-WC-050	TBD	Once per month during removal activities	1/10	0	0	0	0	TBD
Waste Water	PCBs, TSS	Low	NC-WC-004, NC-GC-007	TBD	Once per week during wastewater treatment	1/10	0	0	0	0	TBD
Waste Water	Phosphorus	Low	NC-WC-050	TBD	Once per month during wastewater treatment	1/10	0	0	0	0	TBD
Sediment	PCBs	Low	NC-GC-038 HN-GC-002	80	Once	8	0	0	0	0	88
Wipe	PCBs	Low	HN-GC-002	TBD	Once	TBD	0	0	0	0	TBD

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	
SP-Othr-3	Surface Wipes, Rev3	EQ	Wipe	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 for wipes, sediment, water	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:

¹The reference letter or number is from the Project Sampling SOP References table (Worksheet #21).

² SMO – Sample Management Office

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 and ALS 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)
NC-MT-012	<i>Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analyses, SW846 Methods 6010B, 6010C, and 200.72/2/11</i>	Definitive	Metals	ICP	Test America-North Canton	N
NC-MT-002	<i>SW 6020A - Inductively Coupled Plasma-Mass Spectrometry EPA6020, 6020A, & 200.8 2/15/11</i>	Definitive	Metals	ICP/MS	Test America-North Canton	N
NC-MT-014	<i>Prep & Analysis of Mercury in Aqueous and Solid Samples by Cold Vapor Atomic Absorption Spectroscopy, March 2013</i>	Definitive	Hg	Cold Vapor Atomic Absorption	Test America-North Canton	N
NC-WC-034	<i>Flashpoint (Closed Cup) ASTM D93-08, SW846 Method 1010, 4/10/12</i>	Definitive	Flashpoint	Pensky-Marten Closed Cup Tester	Test America-North Canton	N
NC-GC-007	<i>Analysis of Pesticides and PCBs EPA608, 5/25/11</i>	Definitive	Pesticides	GC/ECD	Test America-North Canton	N
NC-WC-050	<i>Phosphorous: Total, Ortho and Organic - EPA365.1 and SM4500P, 10/20/10</i>	Definitive	Total Phosphorus	Spectrophotometer	Test America-North Canton	N
NC-WC-004	<i>Total Solids, Percent Moisture, Total Settleable Solids, Ash, and Total Volatile Solids, 4/23/12</i>	Definitive	TSS	Drying Oven/Analytical Balance	Test America-North Canton	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)
NC-GC-038	<i>Gas Chromatographic Analysis Based on Methods 8000B, 8021B, 8081A, 8081B, 8082, 8082A, 8151A, 8015B, 8015C, and 615, 5/1/11</i>	Definitive	PCB	GC/ECD	Test America-North Canton	N
NC-MS-019	<i>Determination of Volatile Organics by GC/MS 8260C, 8260B, and 8260A, 6/29/12</i>	Definitive	VOCs	GC/MS	Test America-North Canton	N
NC-MS-018	<i>GC/MS Analysis Based on Method 8270C, 10/26/10</i>	Definitive	SVOC	GC/MS	Test America-North Canton	N
NC-GC-038	<i>Gas Chromatographic Analysis Based on Methods 8000B, 8021B, 8081A, 8081B, 8082, 8082A, 8151A, 8015B, 8015C, and 615, 5/1/11</i>	Definitive	Pesticides	GC/ECD	Test America-North Canton	N
SOP Herbicides SAV	<i>Chlorinated Herbicides by GC/ECD, 1/6/11</i>	Definitive	Herbicides	GC/ECD	Test America-Savannah	N
NC-WC-010	<i>pH Electrometric Method SW9040B, SW9045C, EPA150.1, 4/16/12</i>	Definitive	pH	pH meter	Test America-North Canton	N
NC-WC-046	<i>Paint Filter SW9095, 8/27/12</i>	Screening	Paint Filter	Paint Filter	Test America-North Canton	N
PE-IHD-002, Rev.1	<i>IH Air Method for Total And Respirable Dusts and Carbon Blank, 8/27/10</i>	Definitive	Total Particulates	Balance	Test America-Phoenix	N
PE-IHD-015, Rev1	<i>IH Air Monitoring Method for Polychlorobiphenyls, 1/28/11</i>	Definitive	PCB	GC/ECD	Test America-Phoenix	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 PE-IHD-008 R.2	<i>IH Air Monitoring Method for Polynuclear Aromatic Hydrocarbons</i> 5/25/12	Definitive	PAH	HPLC	Test America-Phoenix	N
SA-GE-085, Rev. 7	<i>Sulfide: Titrimetric Preparation and Analysis</i> , 6/9/11	Definitive	Total Sulfide	N/A	Test America-Savannah	N
NC-WC-032	<i>Cyanide, Preparation Method SW9012A, EPA335.1, 335.2, SM4500CN-I, SM4500CN-E, CLP ILM03.0</i> , 4/16/12	Definitive	Total Cyanide	Systea Easy Chem Discrete Analyzer	Test America-North Canton	N
HN-GC-002-R06	<i>Polychlorinated Biphenyls</i> , 3/1/13	Definitive	PCB	GC/ECD	ALS-Holland	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	$r \geq 0.995$	Repeat ICAL, if fail remake standards	Test America Analyst	NC-MT-002
	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	$r \geq 0.995$	Repeat ICAL, if fail remake standards	Test America Analyst	NC-MT-012.0
	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	$r \geq 0.995$	Repeat ICAL, if fail re-digest standards and samples	Test America Analyst	NC-MT-014
	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 $r \geq 0.99$	Repeat ICAL, if still fails re-pre standards	Test America Analyst	NC-GC-038 NC-GC-038
	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 $r \geq 0.99$	Repeat ICAL, if still fails re-pre standards	Test America Analyst	NC-GC-038 NC-GC-038
	ICV	After ICAL, prior to sample analysis	$\pm 30\% D$	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	$\pm 15\% D$	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 $r \geq 0.99$	Repeat ICAL, if still fails re-pre standards	Test America Analyst	SOP Herbicides SAV
	ICV	After ICAL, prior to sample analysis	Avg. $\pm 15\% D$, 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. $\pm 15\% D$, 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	NC-MS-019, NC-MS-018,
	ICV	After ICAL, prior to sample analysis	$\pm 20\% D$	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	
Spectrophotometer	ICAL	Prior to first samples analyzed and only when necessary	$r \geq 0.995$	Repeat analysis, re-prep standards	Test America Analyst	NC-WC-050
	ICV	After ICAL	$\pm 10\% D$	Repeat analysis, re-prep standards	Test America Analyst	
	CCV	After every 10 samples and at end of run	$\pm 10\% D$	Repeat analysis, re-prep standards	Test America Analyst	
Pensky-Marten Closed Cup	ICAL	Prior to first samples analyzed and 1 per batch	27.2 $\pm 2^{\circ}C$	Repeat analysis, re-prep standards	Test America Analyst	NC-WC-034

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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	$r \geq 0.995$	Repeat analysis, re-prep standards	Test America Analyst	NC-WC-032
	ICV	After ICAL	$\pm 10\% D$	Repeat analysis, re-prep standards	Test America Analyst	
	CCV	After every 10 samples and at end of run	$\pm 10\% D$	Repeat analysis, re-prep standards	Test America Analyst	
pH Meter	ICAL	Prior to sample analysis			Test America Analyst	NC-WC-010
	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; Ethylbenzene; Vinyl chloride

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

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					NC-MT-002
			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					NC-MT-012.
	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					NC-MT-014

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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					NC-MS-019, NC-MS-018, NC-GC-038 NC-GC-038, NC-GC-038, 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.					NC-WC-010
Flashpoint	Clean and rinse test cup.			After each sample.					NC-WC-034

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

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.

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.

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/NC-WC- 004					
Sampler's Name	ERRS					
Field Sampling Organization	EQ					
Analytical Organization	Test America- North Canton					
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 \leq 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

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/NC-GC-007					
Sampler's Name	ERRS					
Field Sampling Organization	EQ					
Analytical Organization	Test America-North Canton					
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 \leq 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 – 10-114% R TCMX – 15-131% 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

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Worksheet #28 – continued

Worksheet #28-3

Matrix	Surface Water/Wastewater					
Analytical Group	Phosphorus					
Concentration Level	Low					
Sampling SOP	Worksheet #17					
Analytical Method/ SOP Reference	4500P/NC-WC-050					
Sampler's Name	ERRS					
Field Sampling Organization	EQ					
Analytical Organization	Test America-North Canton					
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 \leq 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	80 to 120 % R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
MS/MSD	1 per batch	65 to 131 % R	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B

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	NC-GC- 038SW846 8082/ NC-GC-038
Sampler's Name	ERRS
Field Sampling Organization	EQ
Analytical Organization	Test America- North Canton
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 \leq 30%	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	62to 120 % R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
LCS-Aroclor 1260	1 per batch	56 to 122 % R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
Surrogates	2 per sample	DCB – 14 to 163 %R TCMX – 29 to 151 %R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
MS-Aroclor 1016	1 per batch	22 to 157 % R	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B
MS-Aroclor 1260	1 per batch	13 to 161 % 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 Reactive Sulfide; North Canton 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.		Matrix Spike			Blank Spike		
		LCL ¹	UCL ²	LCL	UCL	RPD	LCL	UCL	RPD
TCLP Metals by 1311/6000/7000 NC-OP-033NC-MT-012.0/NC-MT-014									
SW 6010B	Arsenic	-	-	80	120	20	80	120	20
SW 6010B	Barium	-	-	80	120	20	80	120	20
SW 6010B	Cadmium	-	-	80	120	20	80	120	20
SW 6010B	Chromium	-	-	80	120	20	80	120	20
SW 6010B	Lead	-	-	80	122	20	80	120	20
SW 6010B	Selenium	-	-	80	120	20	80	120	20
SW 6010B	Silver	-	-	80	121	20	80	123	20
SW 7470A	Mercury	-	-	64	130	20	72	128	20
TCLP Pesticides by EPA Method 1311/8081A NC-OP-033NC-GC-038NC-GC-038SW846 8086/ NC-GC-038, REV.2									
SW 8081	Methoxychlor			42	141	30	50	150	50
SW 8081	gamma-BHC (Lindane)			59	137	30	50	150	50
SW 8081	Chlordane								
SW 8081	Endrin			59	136	30	50	150	50
SW 8081	Heptachlor			63	123	30	50	150	50
SW 8081	Heptachlor epoxide			59	141	30	50	150	50
SW 8081	Toxaphene								
SW 8081	Tetrachloro-meta-xylene	46	122						
SW 8081	Decachlorobiphenyl	34	141						
TCLP Volatile Organic Compounds by EPA Method 1311/8260B NC-OP-033NC-MS-019SW846 8086/ NC-MS-019, REV.2									
SW 8260B	Benzene			84	120	30	85	119	30
SW 8260B	2-Butanone (MEK)			49	120	30	49	117	30
SW 8260B	Carbon tetrachloride			54	122	30	60	110	30
SW 8260B	Chlorobenzene			86	111	30	85	113	30
SW 8260B	Chloroform			87	123	30	86	124	30
SW 8260B	1,2-Dichloroethane			71	133	30	67	139	30
SW 8260B	1,1-Dichloroethene			81	114	30	80	115	30
SW 8260B	Tetrachloroethene			79	134	30	74	138	30
SW 8260B	Trichloroethene			78	130	30	75	134	30
SW 8260B	Vinyl chloride			56	111	30	51	118	30
SW 8260B	1,2-Dichloroethane-d4	84	128			30			30

Worksheet #28 – continued

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

Method	Analyte	Surr.		Matrix Spike			Blank Spike		
		LCL ¹	UCL ²	LCL	UCL	RPD	LCL	UCL	RPD
SW 8260B	Dibromofluoromethane	80	121			30			30
SW 8260B	Toluene-d8	90	115			30			30
SW 8260B	4-Bromofluorobenzene	70	124			30			30
TCLP Semivolatile Compounds by EPA Method 1311/8270C NC-OP-033NC-MS-018SW846 8086/ NC-MS-018, REV.2									
SW 8270C	1,4-Dichlorobenzene			16	110	30	18	110	30
SW 8270C	2,4-Dinitrotoluene			49	110	30	26	110	30
SW 8270C	Hexachlorobenzene			44	110	30	34	110	30
SW 8270C	Hexachlorobutadiene			35	110	30	26	110	30
SW 8270C	Hexachloroethane			34	110	30	20	110	30
SW 8270C	2-Methylphenol (o-Cresol)			36	114	30	29	110	30
SW 8270C	3&4-Methylphenol (m&p Cresol)			38	110	30	27	110	30
SW 8270C	Nitrobenzene			43	110	30	33	110	30
SW 8270C	Pentachlorophenol			10	122	30	10	131	30
SW 8270C	Pyridine			34	110	30	15	110	30
SW 8270C	2,4,5-Trichlorophenol			35	110	30	26	110	30
SW 8270C	2,4,6-Trichlorophenol			36	110	30	16	110	30
SW 8270C	2-Fluorophenol	27	110						
SW 8270C	Phenol-d6	10	110						
SW 8270C	Nitrobenzene-d5	15	110						
SW 8270C	2-Fluorobiphenyl	27	110						
SW 8270C	2,4,6-Tribromophenol	20	110						
SW 8270C	Terphenyl-d14	38	110						
General Chemistry Parameters									
SW 1010(Mod)/ NC-WC-034	Ignitability by Flashpoint			97	103				
SW 9012/ NC- WC-032	Cyanide, Total			68	123	20	50	134	20
SW 9034/ SOP Sulfide Soil SAV	Sulfide, Total								
SW 9045D/ NC- WC-010	pH			97	103	20			
SW 9095B/ NC- WC-046	Paint Filter Liquids	-		-		-	-		-

1-UCL=Upper Control Limit

2-LCL=Lower Control Limit

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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- North Canton
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.		Matrix Spike			Blank Spike		
		LCL	UCL	LCL	UCL	RPD	LCL	UCL	RPD
Total MetalsNC-MT-012/NC-MT-002/NC-MT-014									
SW 6010B	Aluminum	-	-	75	125	20	80	120	20
SW 6010B	Arsenic	-	-	75	125	20	80	120	20
SW 6010B	Barium	-	-	75	125	20	80	120	20
SW 6010B	Beryllium	-	-	75	125	20	80	120	20
SW 6010B	Cadmium	-	-	75	125	20	80	120	20
SW 6010B	Calcium	-	-	75	125	20	80	120	20
SW 6010B	Chromium	-	-	75	125	20	80	120	20
SW 6010B	Cobalt	-	-	75	125	20	80	120	20
SW 6010B	Iron	-	-	75	125	20	80	120	20
SW 6010B	Lead	-	-	75	125	20	80	120	20
SW 6010B	Magnesium	-	-	75	125	20	80	120	20
SW 6010B	Nickel	-	-	75	125	20	80	120	20
SW 6010B	Potassium	-	-	75	125	20	80	120	20
SW 6010B	Selenium	-	-	75	125	20	80	120	20
SW 6010B	Silver	-	-	75	125	20	80	120	20
SW 6010B	Sodium	-	-	75	125	20	80	120	20
SW 6010B	Vanadium	-	-	75	125	20	80	120	20
SW 6010B	Zinc	-	-	75	125	20	80	120	20
SW 6020A	Antimony	-	-	75	125	20	80	120	20
SW 6020A	Arsenic	-	-	75	125	20	80	120	20
SW 6020A	Copper	-	-	75	125	20	80	120	20
SW 6020A	Manganese	-	-	75	125	20	80	120	20
SW 6020A	Silver	-	-	75	125	20	80	120	20
SW 6020A	Thallium	-	-	75	125	20	80	120	20
SW 7471B	Mercury	-	-	75	125	20	80	120	20
Organochlorine Pesticides NC-GC-038NC-GC-038									
SW 8081	Aldrin	-	-	33	139	30	52	119	30
SW 8081	alpha-BHC	-	-	27	152	30	50	129	30
SW 8081	beta-BHC	-	-	10	199	30	51	127	30
SW 8081	gamma-BHC (Lindane)	-	-	33	146	30	41	137	30
SW 8081	delta-BHC	-	-	14	174	30	54	134	30
SW 8081	Chlordane	-	-						

Worksheet #28 – continued

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

Method	Analyte	Surr.		Matrix Spike			Blank Spike		
		LCL	UCL	LCL	UCL	RPD	LCL	UCL	RPD
SW 8081	alpha-Chlordane	-	-	15	168	30	43	130	30
SW 8081	gamma-Chlordane	-	-	10	188	30	53	129	30
SW 8081	Endrin ketone	-	-	16	183	30	39	137	30
SW 8081	Dieldrin	-	-	35	155	30	45	140	30
SW 8081	4,4'-DDD	-	-	27	177	30	38	160	30
SW 8081	4,4'-DDE	-	-	17	174	30	41	137	30
SW 8081	4,4'-DDT	-	-	24	161	30	34	139	30
SW 8081	Endosulfan I	-	-	10	124	30	13	110	30
SW 8081	Endosulfan II	-	-	12	125	30	22	115	30
SW 8081	Endosulfan sulfate	-	-	12	188	30	44	143	30
SW 8081	Endrin	-	-	25	168	30	48	143	30
SW 8081	Endrin aldehyde	-	-	15	146	30	31	126	30
SW 8081	Heptachlor	-	-	24	153	30	37	127	30
SW 8081	Heptachlor epoxide	-	-	22	179	30	53	132	30
SW 8081	Methoxychlor	-	-	20	183	30	33	151	30
SW 8081	Toxaphene	-	-						
SW 8081	Tetrachloro-meta-xylene	24	150		-				
SW 8081	Decachlorobiphenyl	32	175		-				
PCBs									
NC-GC-038									
SW 8082	PCB-1016	-	-	22	157	30	62	120	30
SW 8082	PCB-1221	-	-		-	-	-	-	
SW 8082	PCB-1232	-	-		-	-	-	-	
SW 8082	PCB-1242	-	-		-	-	-	-	
SW 8082	PCB-1248	-	-		-	-	-	-	
SW 8082	PCB-1254	-	-		-	-	-	-	
SW 8082	PCB-1260	-	-	13	161	30	56	122	30
SW 8082	Tetrachloro-meta-xylene	29	151		-	-	-	-	
SW 8082	Decachlorobiphenyl	14	163		-	-	-	-	
Herbicides by EPA Method 8151A									
SOP Herbicide SAV									
SW8151A	2,4,5-T			32	130	50	32	130	50
SW8151A	2,4-D			47	130	50	47	130	50
SW8151A	2,4-DB	-	-	-	-	-	-	-	-
SW8151A	Dalapon	-	-	-	-	-	-	-	-
SW8151A	Dicamba	-	-	-	-	-	-	-	-

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Worksheet #28 – continued

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

Method	Analyte	Surr.		Matrix Spike			Blank Spike		
		LCL	UCL	LCL	UCL	RPD	LCL	UCL	RPD
SW8151A	Dichlorprop								
SW8151A	Dinoseb			10	130	50	10	130	50
SW8151A	MCPA								
SW8151A	Mecoprop								
SW8151A	Pentachlorophenol			50	130	50	50	130	50
SW8151A	Silvex (2,4,5-TP)			24	130	50	24	130	50
SW8151A	DCAA	35	137						
Volatile Organic Compounds by GC/MS NC-MS-019									
SW 8260A	Acetone	-	-	24	140	30	41	137	30
SW 8260A	Acrolein	-	-	10	149	30	52	146	30
SW 8260A	Acrylonitrile	-	-	40	132	30	62	127	30
SW 8260A	Allyl chloride	-	-						
SW 8260A	Benzene	-	-	53	118	30	79	112	30
SW 8260A	Bromobenzene	-	-	24	144	30	81	115	30
SW 8260A	Bromochloromethane	-	-	53	116	30	79	111	30
SW 8260A	Bromodichloromethane (Dichlorobromomethane)	-	-	35	132	30	84	122	30
SW 8260A	Bromoform	-	-	18	129	30	62	133	30
SW 8260A	Bromomethane (Methyl bromide)	-	-	33	130	30	42	136	30
SW 8260A	2-Butanone (MEK)	-	-	30	143	30	52	131	30
SW 8260A	tert-Butylbenzene	-	-	10	163	30	76	126	30
SW 8260A	sec-Butylbenzene	-	-	10	172	30	74	129	30
SW 8260A	n-Butylbenzene	-	-	10	148	30	68	135	30
SW 8260A	Carbon disulfide	-	-	20	151	30	62	146	30
SW 8260A	Carbon tetrachloride	-	-	32	137	30	71	129	30
SW 8260A	Chlorobenzene	-	-	37	116	30	78	110	30
SW 8260A	Chloroethane	-	-	45	118	30	58	117	30
SW 8260A	2-Chloroethylvinyl ether	-	-	10	162	30	28	173	30
SW 8260A	Chloroform	-	-	53	119	30	77	114	30
SW 8260A	Chloromethane (Methyl chloride)	-	-	34	117	30	50	110	30
SW 8260A	Chloroprene	-	-						
SW 8260A	4-Chlorotoluene	-	-	15	149	30	79	118	30
SW 8260A	2-Chlorotoluene	-	-	11	162	30	78	119	30
SW 8260A	Cyclohexane	-	-	28	118	30	66	110	30

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Worksheet #28 – continued

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

Method	Analyte	Surr.		Matrix Spike			Blank Spike		
		LCL	UCL	LCL	UCL	RPD	LCL	UCL	RPD
SW 8260A	Dibromochloromethane (Chlorodibromomethane)	-	-	56	118	30	64	119	30
SW 8260A	1,2-Dibromo-3-chloropropane	-	-	10	153	30	61	132	30
SW 8260A	1,2-Dibromoethane (EDB)	-	-	45	127	30	83	117	30
SW 8260A	Dibromomethane	-	-	52	123	30	85	120	30
SW 8260A	trans-1,4-Dichloro-2-butene	-	-	70	130	30	70	130	30
SW 8260A	1,2-Dichlorobenzene	-	-	17	122	30	76	110	30
SW 8260A	1,4-Dichlorobenzene	-	-	15	121	30	75	110	30
SW 8260A	1,3-Dichlorobenzene	-	-	16	126	30	78	111	30
SW 8260A	Dichlorodifluoromethane	-	-	17	115	30	26	113	30
SW 8260A	1,1-Dichloroethane	-	-	54	122	30	76	115	30
SW 8260A	1,2-Dichloroethane	-	-	49	123	30	72	120	30
SW 8260A	cis-1,2-Dichloroethene	-	-	50	119	30	76	113	30
SW 8260A	trans-1,2-Dichloroethene	-	-	50	123	30	78	117	30
SW 8260A	1,2-Dichloroethene (total)	-	-	51	120	30	78	115	30
SW 8260A	1,1-Dichloroethene	-	-	49	157	30	75	135	30
SW 8260A	1,3-Dichloropropane	-	-	54	128	30	82	118	30
SW 8260A	2,2-Dichloropropane	-	-	49	132	30	69	135	30
SW 8260A	1,2-Dichloropropane	-	-	61	117	30	87	113	30
SW 8260A	1,1-Dichloropropene	-	-						
SW 8260A	cis-1,3-Dichloropropene	-	-	27	133	30	74	128	30
SW 8260A	1,3-Dichloropropene (total)	-	-			30			30
SW 8260A	trans-1,3-Dichloropropene	-	-	28	137	30	73	131	30
SW 8260A	Diethyl ether	-	-	70	130	30	70	130	30
SW 8260A	Ethyl acetate	-	-			30			30
SW 8260A	Ethylbenzene	-	-	30	131	30	79	117	30
SW 8260A	Ethyl methacrylate	-	-			30			30
SW 8260A	Hexachlorobutadiene	-	-	10	131	30	54	131	30
SW 8260A	n-Hexane	-	-	26	151	30	86	134	30
SW 8260A	2-Hexanone	-	-	37	147	30	64	136	30
SW 8260A	Iodomethane	-	-	51	132	30	79	130	30
SW 8260A	Isopropylbenzene (Cumene)	-	-	21	134	30	76	122	30
SW 8260A	p-Isopropyltoluene	-	-	10	165	30	77	131	30
SW 8260A	Methacrylonitrile	-	-			30			30
SW 8260A	Methyl tert-butyl ether	-	-	51	157	30	49	165	30

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Worksheet #28 – continued

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

Method	Analyte	Surr.		Matrix Spike			Blank Spike		
		LCL	UCL	LCL	UCL	RPD	LCL	UCL	RPD
SW 8260A	Methylene chloride	-	-	54	115	30	75	118	30
SW 8260A	Methyl methacrylate	-	-			30			30
SW 8260A	2-Methylnaphthalene	-	-			30			30
SW 8260A	4-Methyl-2-pentanone (MIBK)	-	-	43	147	30	67	135	30
SW 8260A	Naphthalene	-	-	10	124	30	65	123	30
SW 8260A	2-Nitropropane	-	-			30			30
SW 8260A	Pentachloroethane	-	-						
SW 8260A	Propionitrile	-	-			30			30
SW 8260A	n-Propylbenzene	-	-	10	178	30	81	129	30
SW 8260A	Styrene	-	-	27	127	30	87	117	30
SW 8260A	1,1,1,2-Tetrachloroethane	-	-	34	135	30	81	119	30
SW 8260A	1,1,2,2-Tetrachloroethane	-	-	16	179	30	77	123	30
SW 8260A	Tetrachloroethene	-	-	31	135	30	79	114	30
SW 8260A	Toluene	-	-	39	129	30	75	111	30
SW 8260A	1,2,3-Trichlorobenzene	-	-	10	110	30	61	121	30
SW 8260A	1,2,4-Trichlorobenzene	-	-	10	111	30	64	124	30
SW 8260A	1,1,1-Trichloroethane	-	-	51	128	30	77	126	30
SW 8260A	1,1,2-Trichloroethane	-	-	10	166	30	83	112	30
SW 8260A	Trichloroethene	-	-	10	177	30	79	113	30
SW 8260A	Trichlorofluoromethane	-	-	36	142	30	57	146	30
SW 8260A	1,2,3-Trichloropropane	-	-	32	174	30	84	126	30
SW 8260A	1,1,2-Trichlorotrifluoroethane	-	-	50	147	30	82	138	30
SW 8260A	1,2,4-Trimethylbenzene	-	-	10	173	30	80	129	30
SW 8260A	1,3,5-Trimethylbenzene	-	-	10	171	30	78	128	30
SW 8260A	Vinyl Acetate	-	-	70	130	30	70	130	30
SW 8260A	Vinyl chloride	-	-	42	117	30	57	114	30
SW 8260A	m,p-Xylene	-	-	29	131	30	80	117	30
SW 8260A	o-Xylene	-	-	29	134	30	80	120	30
SW 8260A	Xylenes, Total	-	-	30	131	30	80	118	30
SW 8260A	1,2-Dichloroethane-d4	58	123		-	-			
SW 8260A	Dibromofluoromethane	37	132		-	-			
SW 8260A	Toluene-d8	67	125		-	-			
SW 8260A	4-Bromofluorobenzene	52	136		-	-			

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Worksheet #28 – continued

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

Method	Analyte	Surr.		Matrix Spike			Blank Spike		
		LCL	UCL	LCL	UCL	RPD	LCL	UCL	RPD
Semivolatile Organics by GC/MS NC-MS-018									
SW 8270C	Acenaphthene	-	-	22	110	99	38	110	30
SW 8270C	Acenaphthylene	-	-	24	110	99	40	110	30
SW 8270C	Acetophenone	-	-	31	110	43	40	110	30
SW 8270C	2-Acetylaminofluorene	-	-						
SW 8270C	4-Aminobiphenyl	-	-						
SW 8270C	Aniline	-	-	10	110	30	23	110	30
SW 8270C	Anthracene	-	-	20	110	99	48	110	30
SW 8270C	Benzo (a) anthracene	-	-	10	122	99	50	110	30
SW 8270C	Benzo (b) fluoranthene	-	-	12	118	99	43	110	30
SW 8270C	Benzo (g,h,i) perylene	-	-	10	117	99	51	110	30
SW 8270C	Benzo (k) fluoranthene	-	-	10	121	99	38	105	30
SW 8270C	Benzo (a) pyrene	-	-	10	110	99	44	110	30
SW 8270C	Benzidine	-	-						
SW 8270C	Benzyl alcohol	-	-	10	142	99	23	110	30
SW 8270C	Bis(2-chloroethoxy)methane	-	-	26	110	37	32	110	30
SW 8270C	Bis(2-chloroethyl)ether	-	-	21	110	55	34	110	30
SW 8270C	Bis(2-chloroisopropyl) ether	-	-	11	110	42	29	110	30
SW 8270C	Bis(2-ethylhexyl)phthalate	-	-	40	110	30	50	110	30
SW 8270C	4-Bromophenyl phenyl ether	-	-	33	110	30	39	110	30
SW 8270C	Butyl benzyl phthalate	-	-	44	110	30	51	110	30
SW 8270C	Carbazole	-	-	34	110	30	50	110	30
SW 8270C	4-Chloroaniline	-	-	10	110	36	30	110	30
SW 8270C	Chlorobenzilate	-	-						
SW 8270C	4-Chloro-3-methylphenol	-	-	25	110	54	48	110	30
SW 8270C	2-Chloronaphthalene	-	-	28	110	30	32	110	30
SW 8270C	2-Chlorophenol	-	-	10	110	47	37	110	30
SW 8270C	4-Chlorophenyl phenyl ether	-	-	32	110	30	40	110	30
SW 8270C	Chrysene	-	-	10	125	99	50	110	30
SW 8270C	Diallate (cis or trans)	-	-						
SW 8270C	Dibenzofuran	-	-	29	110	30	43	110	30
SW 8270C	1,2-Dichlorobenzene	-	-	25	110	40	32	110	30
SW 8270C	Dibenz (a,h) anthracene	-	-	14	113	99	51	110	30
SW 8270C	1,3-Dichlorobenzene	-	-	24	110	48	29	110	30

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Worksheet #28 – continued

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

Method	Analyte	Surr.		Matrix Spike			Blank Spike		
		LCL	UCL	LCL	UCL	RPD	LCL	UCL	RPD
SW 8270C	1,4-Dichlorobenzene	-	-	28	110	43	33	110	30
SW 8270C	Di-n-butyl phthalate	-	-	43	110	30	51	110	30
SW 8270C	1,2-Diphenylhydrazine	-	-						
SW 8270C	3,3'-Dichlorobenzidine	-	-	10	110	56	28	110	30
SW 8270C	2,4-Dichlorophenol	-	-	10	110	34	39	110	30
SW 8270C	2,6-Dichlorophenol	-	-						
SW 8270C	Diethyl phthalate	-	-	42	110	30	52	110	30
SW 8270C	7,12-Dimethylbenz (a) anthracene	-	-						
SW 8270C	Dimethoate	-	-						
SW 8270C	Dimethylaminoazobenzene	-	-						
SW 8270C	3,3'-Dimethylbenzidine	-	-						
SW 8270C	2,4-Dimethylphenol	-	-	10	110	31	29	110	30
SW 8270C	Dimethyl phthalate	-	-	41	110	30	50	110	30
SW 8270C	1,3-Dinitrobenzene	-	-						
SW 8270C	4,6-Dinitro-2-methylphenol	-	-	10	110	55	10	110	30
SW 8270C	2,4-Dinitrophenol	-	-	10	110	99	10	110	30
SW 8270C	2,6-Dinitrotoluene	-	-	35	110	30	45	110	30
SW 8270C	Di-n-octyl phthalate	-	-	24	119	30	48	110	30
SW 8270C	Diphenylamine	-	-						
SW 8270C	Disulfoton	-	-						
SW 8270C	Ethyl methanesulfonate	-	-						
SW 8270C	Famphur	-	-						
SW 8270C	Fluoranthene	-	-	10	110	99	51	110	30
SW 8270C	Fluorene	-	-	23	110	99	46	110	30
SW 8270C	Hexachlorobenzene	-	-	34	110	30	43	110	30
SW 8270C	Hexachlorobutadiene	-	-	25	110	34	29	110	30
SW 8270C	Hexachlorocyclopentadiene	-	-	10	110	79	12	110	30
SW 8270C	Hexachloroethane	-	-	12	110	50	30	110	30
SW 8270C	Hexachloropropene	-	-						
SW 8270C	Indeno (1,2,3-cd) pyrene	-	-	10	114	99	50	110	30
SW 8270C	Isodrin	-	-						
SW 8270C	Isophorone	-	-	29	110	38	36	110	30
SW 8270C	Isosafrole	-	-						
SW 8270C	Kepone	-	-						

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Worksheet #28 – continued

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

Method	Analyte	Surr.		Matrix Spike			Blank Spike		
		LCL	UCL	LCL	UCL	RPD	LCL	UCL	RPD
SW 8270C	Methapyrilene	-	-						
SW 8270C	3-Methylcholanthrene	-	-						
SW 8270C	1-Methylnaphthalene	-	-	10	122	41	37	110	30
SW 8270C	Methyl methanesulfonate	-	-						
SW 8270C	2-Methylnaphthalene	-	-	10	133	42	36	110	30
SW 8270C	2-Methylphenol (o-Cresol)	-	-	24	110	51	41	110	30
SW 8270C	3&4-Methylphenol (m&p Cresol)	-	-	25	110	50	40	110	30
SW 8270C	Naphthalene	-	-	10	111	99	36	110	30
SW 8270C	1,4-Naphthoquinone	-	-						
SW 8270C	1-Naphthylamine	-	-						
SW 8270C	2-Naphthylamine	-	-						
SW 8270C	2-Nitroaniline	-	-	39	110	31	45	110	30
SW 8270C	3-Nitroaniline	-	-	10	110	30	44	110	30
SW 8270C	4-Nitroaniline	-	-	10	110	48	48	110	30
SW 8270C	Nitrobenzene	-	-	23	110	41	32	110	30
SW 8270C	2-Nitrophenol	-	-	10	110	49	34	110	30
SW 8270C	4-Nitrophenol	-	-	10	113	49	28	110	30
SW 8270C	5-Nitro-o-toluidine	-	-						
SW 8270C	N-Nitrosodi-n-butylamine	-	-						
SW 8270C	N-Nitrosodiethylamine	-	-						
SW 8270C	N-Nitrosodimethylamine	-	-	20	110	46	31	110	30
SW 8270C	N-Nitrosomethylethylamine	-	-						
SW 8270C	N-Nitrosodiphenylamine	-	-	22	110	30	46	110	30
SW 8270C	N-Nitrosodi-n-propylamine	-	-	26	110	42	38	110	30
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	-	-	10	110	50	10	110	30
SW 8270C	Pentachloronitrobenzene	-	-						
SW 8270C	Phenacetin	-	-						
SW 8270C	Phenanthrene	-	-	10	166	99	49	110	30

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Worksheet #28 – continued

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

Method	Analyte	Surr.		Matrix Spike			Blank Spike		
		LCL	UCL	LCL	UCL	RPD	LCL	UCL	RPD
SW 8270C	Phenol	-	-	17	110	53	38	110	30
SW 8270C	1,4-Phenylenediamine	-	-						
SW 8270C	Phorate	-	-						
SW 8270C	2-Picoline	-	-						
SW 8270C	Pronamide	-	-						
SW 8270C	Pyrene	-	-	10	147	99	49	110	30
SW 8270C	Pyridine	-	-	10	110	52	22	110	30
SW 8270C	Safrole	-	-						
SW 8270C	Sulfotepp	-	-						
SW 8270C	1,2,4,5-Tetrachlorobenzene	-	-						
SW 8270C	2,3,4,6-Tetrachlorophenol	-	-						
SW 8270C	Thionazin	-	-						
SW 8270C	o-Toluidine	-	-						
SW 8270C	1,2,4-Trichlorobenzene	-	-	27	110	34	28	110	30
SW 8270C	2,4,5-Trichlorophenol	-	-	10	117	99	25	110	30
SW 8270C	2,4,6-Trichlorophenol	-	-	10	110	38	12	110	30
SW 8270C	O,O,O-Triethyl phosphorothioate	-	-						
SW 8270C	1,3,5-Trinitrobenzene	-	-						
SW 8270C	2-Fluorophenol	24	110		-	-	-	-	
SW 8270C	Phenol-d6	26	110		-	-	-	-	
SW 8270C	Nitrobenzene-d5	20	110		-	-	-	-	
SW 8270C	2-Fluorobiphenyl	24	110		-	-	-	-	
SW 8270C	2,4,6-Tribromophenol	10	110		-	-	-	-	
SW 8270C	Terphenyl-d14	36	110		-	-	-	-	

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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- North Canton
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 28-7a	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 28-7a	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
Surrogates	See Table 28-7a	See Table 28-7a	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B
MS/MSD	1 per batch	See Table 28-7a	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.		Matrix Spike			Blank Spike		
		LCL	UCL	LCL	UCL	RPD	LCL	UCL	RPD
Total Metals									
NC-MT-012.0/NC-MT-002/NC-MT-014									
SW 6010B	Aluminum	-	-	75	125	20	80	120	20
SW 6010B	Arsenic	-	-	75	125	20	80	120	20
SW 6010B	Barium	-	-	75	125	20	80	120	20
SW 6010B	Beryllium	-	-	75	125	20	80	120	20
SW 6010B	Cadmium	-	-	75	125	20	80	120	20
SW 6010B	Calcium	-	-	75	125	20	80	120	20
SW 6010B	Chromium	-	-	75	125	20	80	120	20
SW 6010B	Cobalt	-	-	75	125	20	80	120	20
SW 6010B	Iron	-	-	75	125	20	80	120	20
SW 6010B	Lead	-	-	75	125	20	80	120	20
SW 6010B	Magnesium	-	-	75	125	20	80	120	20
SW 6010B	Nickel	-	-	75	125	20	80	120	20
SW 6010B	Potassium	-	-	75	125	20	80	120	20
SW 6010B	Selenium	-	-	75	125	20	80	120	20
SW 6010B	Silver	-	-	75	125	20	80	120	20
SW 6010B	Sodium	-	-	75	125	20	80	120	20
SW 6010B	Vanadium	-	-	75	125	20	80	120	20
SW 6010B	Zinc	-	-	75	125	20	80	120	20
SW 6020A	Antimony	-		75	125	20	80	120	20
SW 6020A	Arsenic	-		75	125	20	80	120	20
SW 6020A	Copper	-		75	125	20	80	120	20
SW 6020A	Manganese	-		75	125	20	80	120	20
SW 6020A	Silver	-		75	125	20	80	120	20
SW 6020A	Thallium	-		75	125	20	80	120	20
SW 7471B	Mercury	-		75	125	20	80	120	20
Organochlorine Pesticides									
NC-GC-038NC-GC-038									
SW 8081	Aldrin	-	-	33	139	30	52	119	30
SW 8081	alpha-BHC	-	-	27	152	30	50	129	30
SW 8081	beta-BHC	-	-	10	199	30	51	127	30
SW 8081	gamma-BHC (Lindane)	-	-	33	146	30	41	137	30

Worksheet #28 – continued

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

SW 8081	delta-BHC	-	-	14	174	30	54	134	30
SW 8081	Chlordane	-	-						
SW 8081	alpha-Chlordane	-	-	15	168	30	43	130	30
SW 8081	gamma-Chlordane	-	-	10	188	30	53	129	30
SW 8081	Endrin ketone	-	-	16	183	30	39	137	30
SW 8081	Dieldrin	-	-	35	155	30	45	140	30
SW 8081	4,4'-DDD	-	-	27	177	30	38	160	30
SW 8081	4,4'-DDE	-	-	17	174	30	41	137	30
SW 8081	4,4'-DDT	-	-	24	161	30	34	139	30
SW 8081	Endosulfan I	-	-	10	124	30	13	110	30
SW 8081	Endosulfan II	-	-	12	125	30	22	115	30
SW 8081	Endosulfan sulfate	-	-	12	188	30	44	143	30
SW 8081	Endrin	-	-	25	168	30	48	143	30
SW 8081	Endrin aldehyde	-	-	15	146	30	31	126	30
SW 8081	Heptachlor	-	-	24	153	30	37	127	30
SW 8081	Heptachlor epoxide	-	-	22	179	30	53	132	30
SW 8081	Methoxychlor	-	-	20	183	30	33	151	30
SW 8081	Toxaphene	-	-	33	139	30	52	119	30
SW 8081	Tetrachloro-meta-xylene	24	150			-	-	-	-
SW 8081	Decachlorobiphenyl	32	175			-	-	-	-
PCBs									
NC-GC-038									
SW 8082	PCB-1016	-	-	22	157	30	62	120	30
SW 8082	PCB-1221	-	-						
SW 8082	PCB-1232	-	-						
SW 8082	PCB-1242	-	-						
SW 8082	PCB-1248	-	-						
SW 8082	PCB-1254	-	-						
SW 8082	PCB-1260	-	-	13	161	30	56	122	30
SW 8082	Tetrachloro-meta-xylene	29	151			-	-	-	-
SW 8082	Decachlorobiphenyl	14	163			-	-	-	-
Herbicides by EPA Method 8151A									
SOP Herbicide SAV									
SW8151A	2,4,5-T			32	130	50	32	130	50
SW8151A	2,4-D			47	130	50	47	130	50
SW8151A	2,4-DB	-	-	-	-	-	-	-	-
SW8151A	Dalapon	-	-	-	-	-	-	-	-
SW8151A	Dicamba	-	-	-	-	-	-	-	-

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Worksheet #28 – continued

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

SW8151A	Dichlorprop	-	-	-	-	-	-	-	-
SW8151A	Dinoseb			10	130	50	10	130	50
SW8151A	MCPA	-	-	-	-	-	-	-	-
SW8151A	Mecoprop	-	-	-	-	-	-	-	-
SW8151A	Pentachlorophenol			50	130	50	50	130	50
SW8151A	Silvex (2,4,5-TP)			24	130	50	24	130	50
SW8151A	DCAA	35	137						
Volatile Organic Compounds by GC/MS NC-MS-019									
SW 8260A	Acetone	-	-	24	140	30	41	137	30
SW 8260A	Acrolein	-	-	10	149	30	52	146	30
SW 8260A	Acrylonitrile	-	-	40	132	30	62	127	30
SW 8260A	Allyl chloride	-	-						
SW 8260A	Benzene	-	-	53	118	30	79	112	30
SW 8260A	Bromobenzene	-	-	24	144	30	81	115	30
SW 8260A	Bromochloromethane	-	-	53	116	30	79	111	30
SW 8260A	Bromodichloromethane (Dichlorobromomethane)	-	-	35	132	30	84	122	30
SW 8260A	Bromoform	-	-	18	129	30	62	133	30
SW 8260A	Bromomethane (Methyl bromide)	-	-	33	130	30	42	136	30
SW 8260A	2-Butanone (MEK)	-	-	30	143	30	52	131	30
SW 8260A	tert-Butylbenzene	-	-	10	163	30	76	126	30
SW 8260A	sec-Butylbenzene	-	-	10	172	30	74	129	30
SW 8260A	n-Butylbenzene	-	-	10	148	30	68	135	30
SW 8260A	Carbon disulfide	-	-	20	151	30	62	146	30
SW 8260A	Carbon tetrachloride	-	-	32	137	30	71	129	30
SW 8260A	Chlorobenzene	-	-	37	116	30	78	110	30
SW 8260A	Chloroethane	-	-	45	118	30	58	117	30
SW 8260A	2-Chloroethylvinyl ether	-	-	10	162	30	28	173	30
SW 8260A	Chloroform	-	-	53	119	30	77	114	30
SW 8260A	Chloromethane (Methyl chloride)	-	-	34	117	30	50	110	30
SW 8260A	Chloroprene	-	-						
SW 8260A	4-Chlorotoluene	-	-	15	149	30	79	118	30
SW 8260A	2-Chlorotoluene	-	-	11	162	30	78	119	30
SW 8260A	Cyclohexane	-	-	28	118	30	66	110	30
SW 8260A	Dibromochloromethane (Chlorodibromomethane)	-	-	56	118	30	64	119	30
SW 8260A	1,2-Dibromo-3-chloropropane	-	-	10	153	30	61	132	30

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Worksheet #28 – continued

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

SW 8260A	1,2-Dibromoethane (EDB)	-	-	45	127	30	83	117	30
SW 8260A	Dibromomethane	-	-	52	123	30	85	120	30
SW 8260A	trans-1,4-Dichloro-2-butene	-	-	70	130	30	70	130	30
SW 8260A	1,2-Dichlorobenzene	-	-	17	122	30	76	110	30
SW 8260A	1,4-Dichlorobenzene	-	-	15	121	30	75	110	30
SW 8260A	1,3-Dichlorobenzene	-	-	16	126	30	78	111	30
SW 8260A	Dichlorodifluoromethane	-	-	17	115	30	26	113	30
SW 8260A	1,1-Dichloroethane	-	-	54	122	30	76	115	30
SW 8260A	1,2-Dichloroethane	-	-	49	123	30	72	120	30
SW 8260A	cis-1,2-Dichloroethene	-	-	50	119	30	76	113	30
SW 8260A	trans-1,2-Dichloroethene	-	-	50	123	30	78	117	30
SW 8260A	1,2-Dichloroethene (total)	-	-	51	120	30	78	115	30
SW 8260A	1,1-Dichloroethene	-	-	49	157	30	75	135	30
SW 8260A	1,3-Dichloropropane	-	-	54	128	30	82	118	30
SW 8260A	2,2-Dichloropropane	-	-	49	132	30	69	135	30
SW 8260A	1,2-Dichloropropane	-	-	61	117	30	87	113	30
SW 8260A	1,1-Dichloropropene	-	-						
SW 8260A	cis-1,3-Dichloropropene	-	-	27	133	30	74	128	30
SW 8260A	1,3-Dichloropropene (total)	-	-			30			30
SW 8260A	trans-1,3-Dichloropropene	-	-	28	137	30	73	131	30
SW 8260A	Diethyl ether	-	-	70	130	30	70	130	30
SW 8260A	Ethyl acetate	-	-			30			30
SW 8260A	Ethylbenzene	-	-	30	131	30	79	117	30
SW 8260A	Ethyl methacrylate	-	-			30			30
SW 8260A	Hexachlorobutadiene	-	-	10	131	30	54	131	30
SW 8260A	n-Hexane	-	-	26	151	30	86	134	30
SW 8260A	2-Hexanone	-	-	37	147	30	64	136	30
SW 8260A	Iodomethane	-	-	51	132	30	79	130	30
SW 8260A	Isopropylbenzene (Cumene)	-	-	21	134	30	76	122	30
SW 8260A	p-Isopropyltoluene	-	-	10	165	30	77	131	30
SW 8260A	Methacrylonitrile	-	-			30			30
SW 8260A	Methyl tert-butyl ether	-	-	51	157	30	49	165	30
SW 8260A	Methylene chloride	-	-	54	115	30	75	118	30
SW 8260A	Methyl methacrylate	-	-			30			30
SW 8260A	2-Methylnaphthalene	-	-			30			30
SW 8260A	4-Methyl-2-pentanone (MIBK)	-	-	43	147	30	67	135	30
SW 8260A	Naphthalene	-	-	10	124	30	65	123	30

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Worksheet #28 – continued

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

SW 8260A	2-Nitropropane	-	-			30			30
SW 8260A	Pentachloroethane	-	-						
SW 8260A	Propionitrile	-	-			30			30
SW 8260A	n-Propylbenzene	-	-	10	178	30	81	129	30
SW 8260A	Styrene	-	-	27	127	30	87	117	30
SW 8260A	1,1,1,2-Tetrachloroethane	-	-	34	135	30	81	119	30
SW 8260A	1,1,2,2-Tetrachloroethane	-	-	16	179	30	77	123	30
SW 8260A	Tetrachloroethene	-	-	31	135	30	79	114	30
SW 8260A	Toluene	-	-	39	129	30	75	111	30
SW 8260A	1,2,3-Trichlorobenzene	-	-	10	110	30	61	121	30
SW 8260A	1,2,4-Trichlorobenzene	-	-	10	111	30	64	124	30
SW 8260A	1,1,1-Trichloroethane	-	-	51	128	30	77	126	30
SW 8260A	1,1,2-Trichloroethane	-	-	10	166	30	83	112	30
SW 8260A	Trichloroethene	-	-	10	177	30	79	113	30
SW 8260A	Trichlorofluoromethane	-	-	36	142	30	57	146	30
SW 8260A	1,2,3-Trichloropropane	-	-	32	174	30	84	126	30
SW 8260A	1,1,2-Trichlorotrifluoroethane	-	-	50	147	30	82	138	30
SW 8260A	1,2,4-Trimethylbenzene	-	-	10	173	30	80	129	30
SW 8260A	1,3,5-Trimethylbenzene	-	-	10	171	30	78	128	30
SW 8260A	Vinyl Acetate	-	-	70	130	30	70	130	30
SW 8260A	Vinyl chloride	-	-	42	117	30	57	114	30
SW 8260A	m,p-Xylene	-	-	29	131	30	80	117	30
SW 8260A	o-Xylene	-	-	29	134	30	80	120	30
SW 8260A	Xylenes, Total	-	-	30	131	30	80	118	30
SW 8260A	1,2-Dichloroethane-d4	58	123	-	-	-	-	-	-
SW 8260A	Dibromofluoromethane	37	132	-	-	-	-	-	-
SW 8260A	Toluene-d8	67	125	-	-	-	-	-	-
SW 8260A	4-Bromofluorobenzene	52	136	-	-	-	-	-	-
Semivolatile Organics by GC/MS									
NC-MS-018									
SW 8270C	Acenaphthene	-	-	22	110	99	38	110	30
SW 8270C	Acenaphthylene	-	-	24	110	99	40	110	30
SW 8270C	Acetophenone	-	-	31	110	43	40	110	30
SW 8270C	2-Acetylaminofluorene	-	-						
SW 8270C	4-Aminobiphenyl	-	-						
SW 8270C	Aniline	-	-	10	110	30	23	110	30
SW 8270C	Cresol(s)	-	-						
SW 8270C	Anthracene	-	-	20	110	99	48	110	30

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Worksheet #28 – continued

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

SW 8270C	Benzo (a) anthracene	-	-	10	122	99	50	110	30
SW 8270C	Benzo (b) fluoranthene	-	-	12	118	99	43	110	30
SW 8270C	Benzo (g,h,i) perylene	-	-	10	117	99	51	110	30
SW 8270C	Benzo (k) fluoranthene	-	-	10	121	99	38	105	30
SW 8270C	Benzo (a) pyrene	-	-	10	110	99	44	110	30
SW 8270C	Benzidine	-	-						
SW 8270C	Benzyl alcohol	-	-	10	142	99	23	110	30
SW 8270C	Bis(2-chloroethoxy)methane	-	-	26	110	37	32	110	30
SW 8270C	Bis(2-chloroethyl)ether	-	-	21	110	55	34	110	30
SW 8270C	Bis(2-chloroisopropyl) ether	-	-	11	110	42	29	110	30
SW 8270C	Bis(2-ethylhexyl)phthalate	-	-	40	110	30	50	110	30
SW 8270C	4-Bromophenyl phenyl ether	-	-	33	110	30	39	110	30
SW 8270C	Butyl benzyl phthalate	-	-	44	110	30	51	110	30
SW 8270C	Carbazole	-	-	34	110	30	50	110	30
SW 8270C	4-Chloroaniline	-	-	10	110	36	30	110	30
SW 8270C	Chlorobenzilate	-	-						
SW 8270C	4-Chloro-3-methylphenol	-	-	25	110	54	48	110	30
SW 8270C	2-Chloronaphthalene	-	-	28	110	30	32	110	30
SW 8270C	2-Chlorophenol	-	-	10	110	47	37	110	30
SW 8270C	4-Chlorophenyl phenyl ether	-	-	32	110	30	40	110	30
SW 8270C	Chrysene	-	-	10	125	99	50	110	30
SW 8270C	Diallate (cis or trans)	-	-						
SW 8270C	Dibenzofuran	-	-	29	110	30	43	110	30
SW 8270C	1,2-Dichlorobenzene	-	-	25	110	40	32	110	30
SW 8270C	Dibenz (a,h) anthracene	-	-	14	113	99	51	110	30
SW 8270C	1,3-Dichlorobenzene	-	-	24	110	48	29	110	30
SW 8270C	1,4-Dichlorobenzene	-	-	28	110	43	33	110	30
SW 8270C	Di-n-butyl phthalate	-	-	43	110	30	51	110	30
SW 8270C	1,2-Diphenylhydrazine	-	-						
SW 8270C	3,3'-Dichlorobenzidine	-	-	10	110	56	28	110	30
SW 8270C	2,4-Dichlorophenol	-	-	10	110	34	39	110	30
SW 8270C	2,6-Dichlorophenol	-	-						
SW 8270C	Diethyl phthalate	-	-	42	110	30	52	110	30
SW 8270C	7,12-Dimethylbenz (a) anthracene	-	-						
SW 8270C	Dimethoate	-	-						
SW 8270C	Dimethylaminoazobenzene	-	-						
SW 8270C	3,3'-Dimethylbenzidine	-	-						

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Worksheet #28 – continued

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

SW 8270C	2,4-Dimethylphenol	-	-	10	110	31	29	110	30
SW 8270C	Dimethyl phthalate	-	-	41	110	30	50	110	30
SW 8270C	1,3-Dinitrobenzene	-	-						
SW 8270C	4,6-Dinitro-2-methylphenol	-	-	10	110	55	10	110	30
SW 8270C	2,4-Dinitrophenol	-	-	10	110	99	10	110	30
SW 8270C	2,6-Dinitrotoluene	-	-	35	110	30	45	110	30
SW 8270C	Di-n-octyl phthalate	-	-	24	119	30	48	110	30
SW 8270C	Diphenylamine	-	-						
SW 8270C	Disulfoton	-	-						
SW 8270C	Ethyl methanesulfonate	-	-						
SW 8270C	Famphur	-	-						
SW 8270C	Fluoranthene	-	-	10	110	99	51	110	30
SW 8270C	Fluorene	-	-	23	110	99	46	110	30
SW 8270C	Hexachlorobenzene	-	-	34	110	30	43	110	30
SW 8270C	Hexachlorobutadiene	-	-	25	110	34	29	110	30
SW 8270C	Hexachlorocyclopentadiene	-	-	10	110	79	12	110	30
SW 8270C	Hexachloroethane	-	-	12	110	50	30	110	30
SW 8270C	Hexachloropropene	-	-						
SW 8270C	Indeno (1,2,3-cd) pyrene	-	-	10	114	99	50	110	30
SW 8270C	Isodrin	-	-						
SW 8270C	Isophorone	-	-	29	110	38	36	110	30
SW 8270C	Isosafrole	-	-						
SW 8270C	Kepone	-	-						
SW 8270C	Methapyrilene	-	-						
SW 8270C	3-Methylcholanthrene	-	-						
SW 8270C	1-Methylnaphthalene	-	-	10	122	41	37	110	30
SW 8270C	Methyl methanesulfonate	-	-						
SW 8270C	2-Methylnaphthalene	-	-	10	133	42	36	110	30
SW 8270C	2-Methylphenol (o-Cresol)	-	-	24	110	51	41	110	30
SW 8270C	3&4-Methylphenol (m&p Cresol)	-	-	25	110	50	40	110	30
SW 8270C	Naphthalene	-	-	10	111	99	36	110	30
SW 8270C	1,4-Naphthoquinone	-	-						
SW 8270C	1-Naphthylamine	-	-						
SW 8270C	2-Naphthylamine	-	-						
SW 8270C	2-Nitroaniline	-	-	39	110	31	45	110	30
SW 8270C	3-Nitroaniline	-	-	10	110	30	44	110	30
SW 8270C	4-Nitroaniline	-	-	10	110	48	48	110	30

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Worksheet #28 – continued

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

SW 8270C	Nitrobenzene	-	-	23	110	41	32	110	30
SW 8270C	2-Nitrophenol	-	-	10	110	49	34	110	30
SW 8270C	4-Nitrophenol	-	-	10	113	49	28	110	30
SW 8270C	5-Nitro-o-toluidine	-	-						
SW 8270C	N-Nitrosodi-n-butylamine	-	-						
SW 8270C	N-Nitrosodiethylamine	-	-						
SW 8270C	N-Nitrosodimethylamine	-	-	20	110	46	31	110	30
SW 8270C	N-Nitrosomethylethylamine	-	-						
SW 8270C	N-Nitrosodiphenylamine	-	-	22	110	30	46	110	30
SW 8270C	N-Nitrosodi-n-propylamine	-	-	26	110	42	38	110	30
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	-	-	10	110	50	10	110	30
SW 8270C	Pentachloronitrobenzene	-	-						
SW 8270C	Phenacetin	-	-						
SW 8270C	Phenanthrene	-	-	10	166	99	49	110	30
SW 8270C	Phenol	-	-	17	110	53	38	110	30
SW 8270C	1,4-Phenylenediamine	-	-						
SW 8270C	Phorate	-	-						
SW 8270C	2-Picoline	-	-						
SW 8270C	Pronamide	-	-						
SW 8270C	Pyrene	-	-	10	147	99	49	110	30
SW 8270C	Pyridine	-	-	10	110	52	22	110	30
SW 8270C	Safrole	-	-						
SW 8270C	Sulfotepp	-	-						
SW 8270C	1,2,4,5-Tetrachlorobenzene	-	-						
SW 8270C	2,3,4,6-Tetrachlorophenol	-	-						
SW 8270C	Thionazin	-	-						
SW 8270C	o-Toluidine	-	-						
SW 8270C	1,2,4-Trichlorobenzene	-	-	27	110	34	28	110	30
SW 8270C	2,4,5-Trichlorophenol	-	-	10	117	99	25	110	30
SW 8270C	2,4,6-Trichlorophenol	-	-	10	110	38	12	110	30
SW 8270C	O,O,O-Triethyl phosphorothioate	-	-						

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Worksheet #28 – continued

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

SW 8270C	1,3,5-Trinitrobenzene	-	-						
SW 8270C	2-Fluorophenol	24	110	-	-	-	-	-	-
SW 8270C	Phenol-d6	26	110			-	-	-	-
SW 8270C	Nitrobenzene-d5	20	110			-	-	-	-
SW 8270C	2-Fluorobiphenyl	24	110			-	-	-	-
SW 8270C	2,4,6-Tribromophenol	10	110			-	-	-	-
SW 8270C	Terphenyl-d14	36	110			-	-	-	-

Worksheet #28 – continued

QAPP Worksheet #28-8

Matrix	Air
Analytical Group	PCBs, PAH & 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 \leq 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

QAPP Worksheet #28-9

Matrix	Sediment-Confirmation					
Analytical Group	PCBs					
Concentration Level	Low					
Sampling SOP	Worksheet #17					
Analytical Method/ SOP Reference	8082/ HN-GC-002-R06					
Sampler's Name	ERRS					
Field Sampling Organization	EQ					
Analytical Organization	ALS-Holland					
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
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 1016/1260	1 per batch	50-130 % R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
Surrogates	2 per sample	DCB – 40-140% R TCMX – 45-124% R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
MS/MSD – Aroclor1016/ 1260	1 per batch	45-124 % R, 50% RPD	Flag associated data as estimated	Chemist	Matrix Interference/ Laboratory Accuracy	See SOP in Appendix B

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QAPP Worksheet #28-10

Matrix	Wipe
Analytical Group	PCBs
Concentration Level	Low
Sampling SOP	Worksheet #17
Analytical Method/ SOP Reference	8082/ HN-GC- 002-R06
Sampler's Name	ERRS
Field Sampling Organization	EQ
Analytical Organization	ALS-Holland
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
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 1016/1260	1 per batch	50-130 % R	Flag associated data as estimated	Chemist	Laboratory Accuracy	See SOP in Appendix B
Surrogates	2 per sample	DCB – 50-130% R TCMX – 50-130% R	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		

QAPP Worksheet #30 Analytical Services Table

Matrix	Analytical Group	Concentration Level	Sample Locations/ID Numbers¹	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 North Canton, OH 45440 Josh McKinney 800-572-9839	2417 Bond Street University Park, IL 60484 708.534.5200
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		
Sediment	PCB	Low/Medium	See Worksheet #19	Worksheet 12- 2 & 12-3	24 Hours	ALS Environmental 3352 128th Avenue Holland, Michigan 49424 616- 738 -7318	
Wipe	PCB	Low/Medium	See Worksheet #19	Worksheet 12- 2 & 12-3	24 Hours		
Air	PCB, PAH 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.

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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.							

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.	Craig Thomas, 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	Craig Thomas, USEPA OSC
Monthly Report	Every month for the prior month activities, as needed	20 th of month for the prior month activities	EQ Response Manager	Craig Thomas, 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	Angye Dragotta, 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
<i>Post-excavation Sampling – Portage Creek Removal Slope Areas</i>			
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.	Angye Dragotta, 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
<i>Surface Soil Sampling – Upjohn Park</i>			
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.	Angye Dragotta , 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
<i>Pre-Removal/Data PCB Gap Sediment Sampling – Portage Creek Select Grids in the Removal Slope Areas</i>			
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.	Angy Dragotta , 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
<i>Waste Characterization Sampling</i>			
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.	Angye Dragotta , 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.	Angye Dragotta, EQM ERRS

Worksheet #35 – continued

Stage/ % Validation	Validation Input	Description	Responsible for Validation
<i>Surface Water Sampling – Portage Creek / Wastewater Treatment Sampling</i>			
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.	Angye Dragotta, 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
<i>Personnel and Area Monitoring Sampling</i>			
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.	Angye Dragotta, 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.	Angye Dragotta, EQM ERRS
<i>Pre- and Post-Construction Sampling – Support Areas</i>			
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.	Angye Dragotta, 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
<i>Borrow Source Sampling - Backfill</i>			
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.	Angye Dragotta, 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

Worksheet #35 – continued

Stage/ % Validation	Validation Input	Description	Responsible for Validation
<i>PCB Wipe Samples</i>			
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.	Angye Dragotta, 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)
<i>Pre-Removal/Data Gap PCB Sampling – Portage Creek Select Grids in the Removal Slope Areas</i>					
IIa / IIb	soil/sediment	PCBs	Medium	U.S. EPA CLP NFG for Organic Data	ERRS / START Chemist
<i>Surface Soil Sampling – Upjohn Park</i>					
IIa / IV	soil	PCBs	Low	U.S. EPA CLP NFG for Organic Data	ERRS / START Chemist
<i>Pre- and Post-Construction Sampling – Support Areas</i>					
IIa / IIb	soils	TCL VOCs, TCL SVOCs, TCL Pesticides, TCL Herbicides, PCBs, TAL metals	Medium	U.S. EPA CLP NFG for Inorganic/Organic Data	ERRS / START Chemist
<i>Waste Characterization Sampling</i>					
IIa	soils	Waste Characterization	High	U.S. EPA CLP NFG for Inorganic/Organic Data	ERRS Chemist
<i>Borrow Source Sampling - Backfill</i>					
IIa / IIb	solids	TCL VOCs, TCL SVOCs, TCL Pesticides, TCL Herbicides, PCBs, TAL metals	Low	U.S. EPA CLP NFG for Inorganic/Organic Data	ERRS / START Chemist
<i>Personnel and Area Monitoring Sampling</i>					
IIa	Air	PCBs, total particulates	Low	U.S. EPA CLP NFG for Inorganic Data	ERRS Chemist
IIa / IIb	surface water	PCBs, TSS, phosphorus	Medium	U.S. EPA CLP NFG for Inorganic Data	ERRS / START Chemist
<i>Post-excavation Sampling – Portage Creek Removal Slope Areas</i>					
IIa / IV	soil/sediment	PCBs	Low	U.S. EPA CLP NFG for Inorganic Data	ERRS / START Chemist

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.

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

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.

References

- ARCADIS. 2009. *Plainwell No. 2 Dam Area Time-Critical Removal Action Final Design Report Allied Paper, Inc./Portage Creek/Kalamazoo river Superfund Site*. 15 July.
- ARCADIS. 2007a. *Multi-Area Quality Assurance Project Plan for the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site*. 29 June.
- ARCADIS BBL. 2007b. *Multi-Area Field Sampling Plan for the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site*. April.
- Weston Solutions, Inc. (Weston). 2011. *Detailed cost Estimate for Removal of Contaminated Sediments in Portage Creek Kalamazoo, Kalamazoo County, Michigan*. 13 April.
- USEPA. 2005a. Intergovernmental Data Quality Task Force. *Uniform Federal Policy for Quality Assurance Project Plans: Evaluation, Assessing, and Documenting Environmental Data Collection and use Programs. Part 1: UFP-QAPP Manual*. Version 1, March 2005. Publication Numbers: USEPA: EPA-505-B-04-900A, Department of Defense: DTIC ADA 427785.
http://www.epa.gov/fedfac/pdf/ufp_qapp_v1_0305.pdf.
- USEPA. 2011. *Request for Approval on a Time-Critical Removal Action and emergency exemption at the Portage Creek Area of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site in Kalamazoo, Kalamazoo County, Michigan*. Date?.
- USEPA Field Environmental Decision Support. 2011a. *Portage Creek Remediation: Volume and Mass Estimations*. 14 April.
- USEPA Field Environmental Decision Support. 2011b. *Portage Creek Core Displays of PCB Concentrations*. 14 April.

APPENDIX A

FIGURES

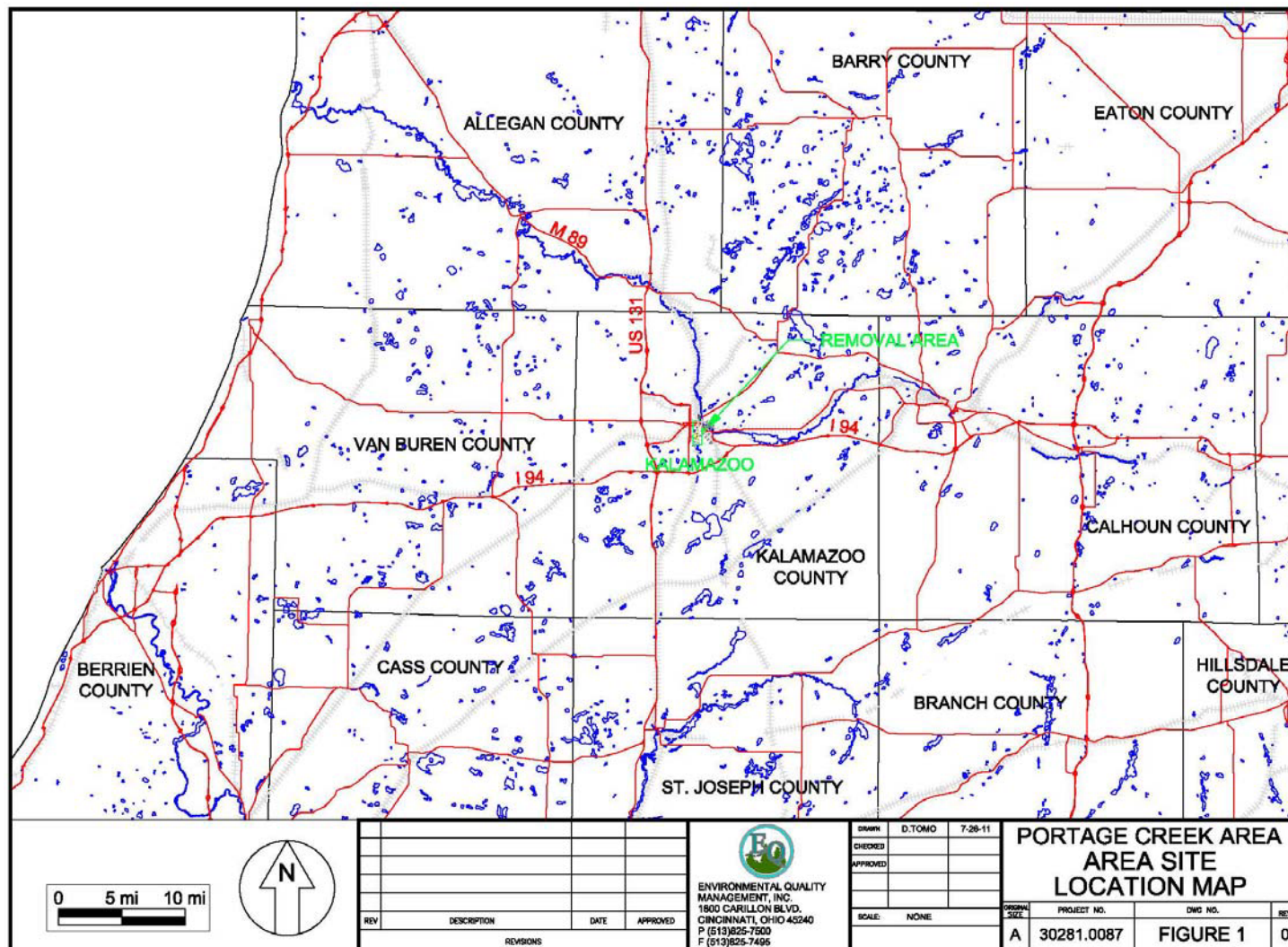


Figure 1. Site Location

3281-87PCA.1

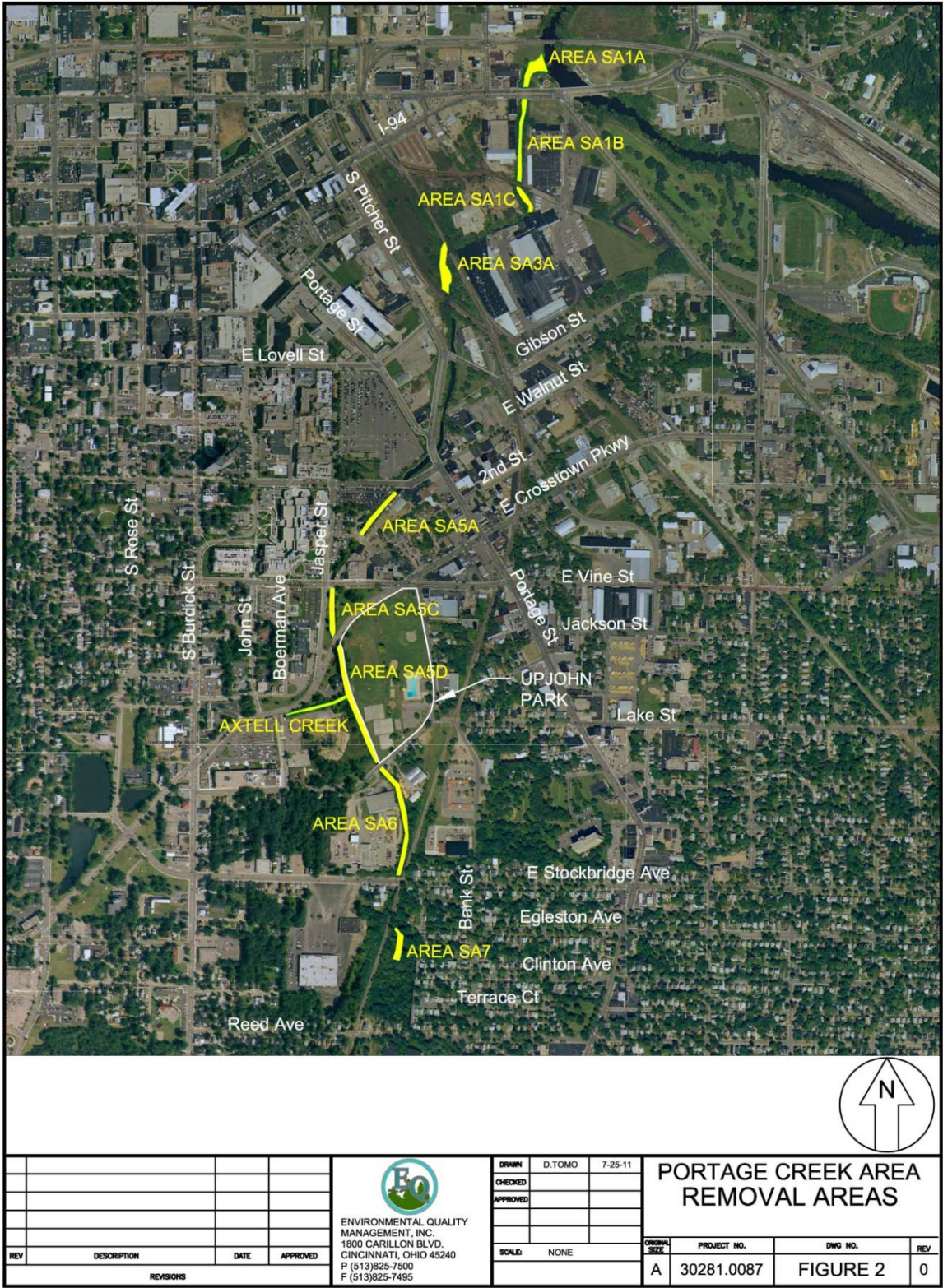


Figure 2. Removal Areas

3281-87PCA.1



Figure 3. Removal Area SA7

3281-87PCA.1

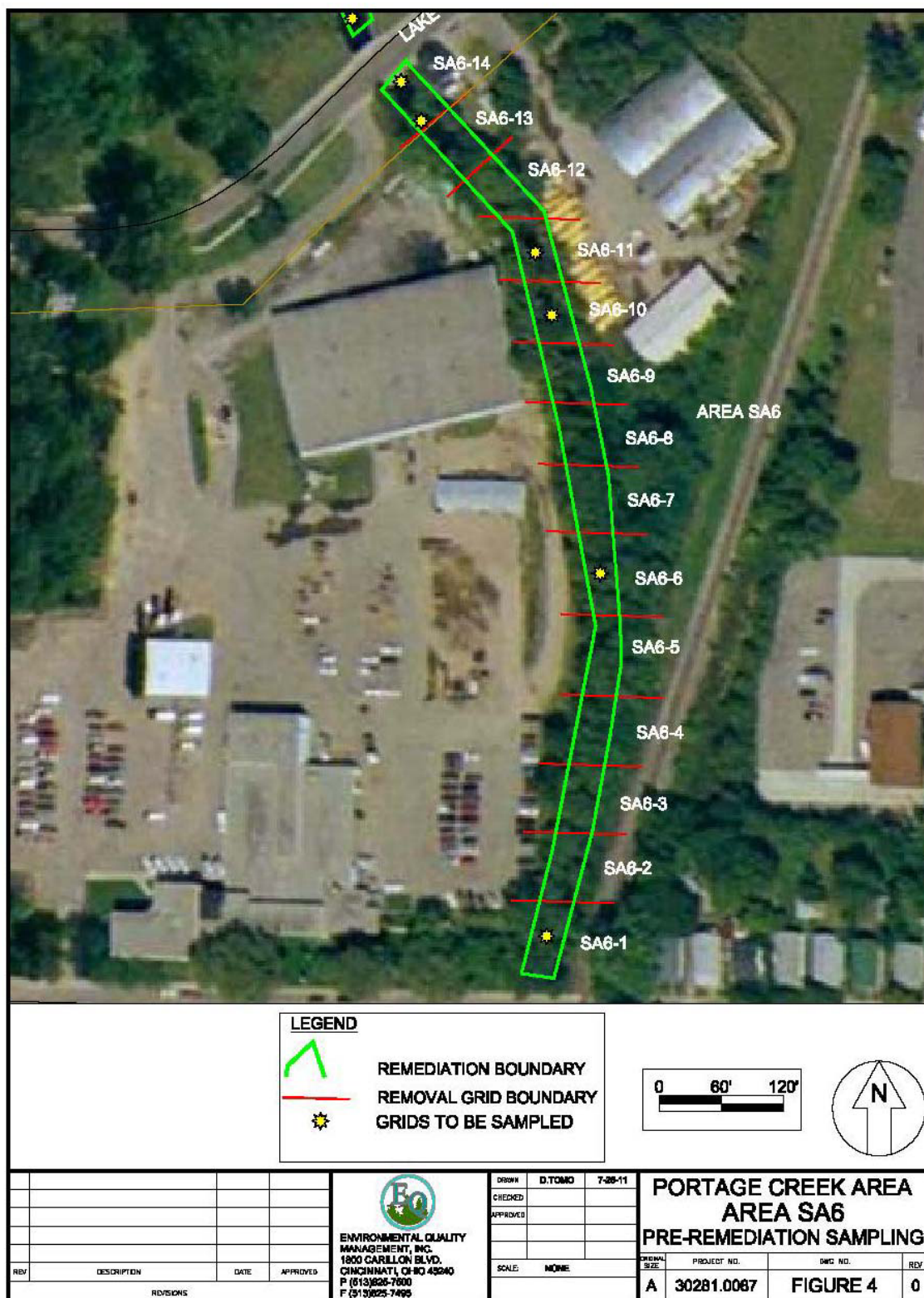


Figure 4. Removal Area SA6

3281-87PCA.1

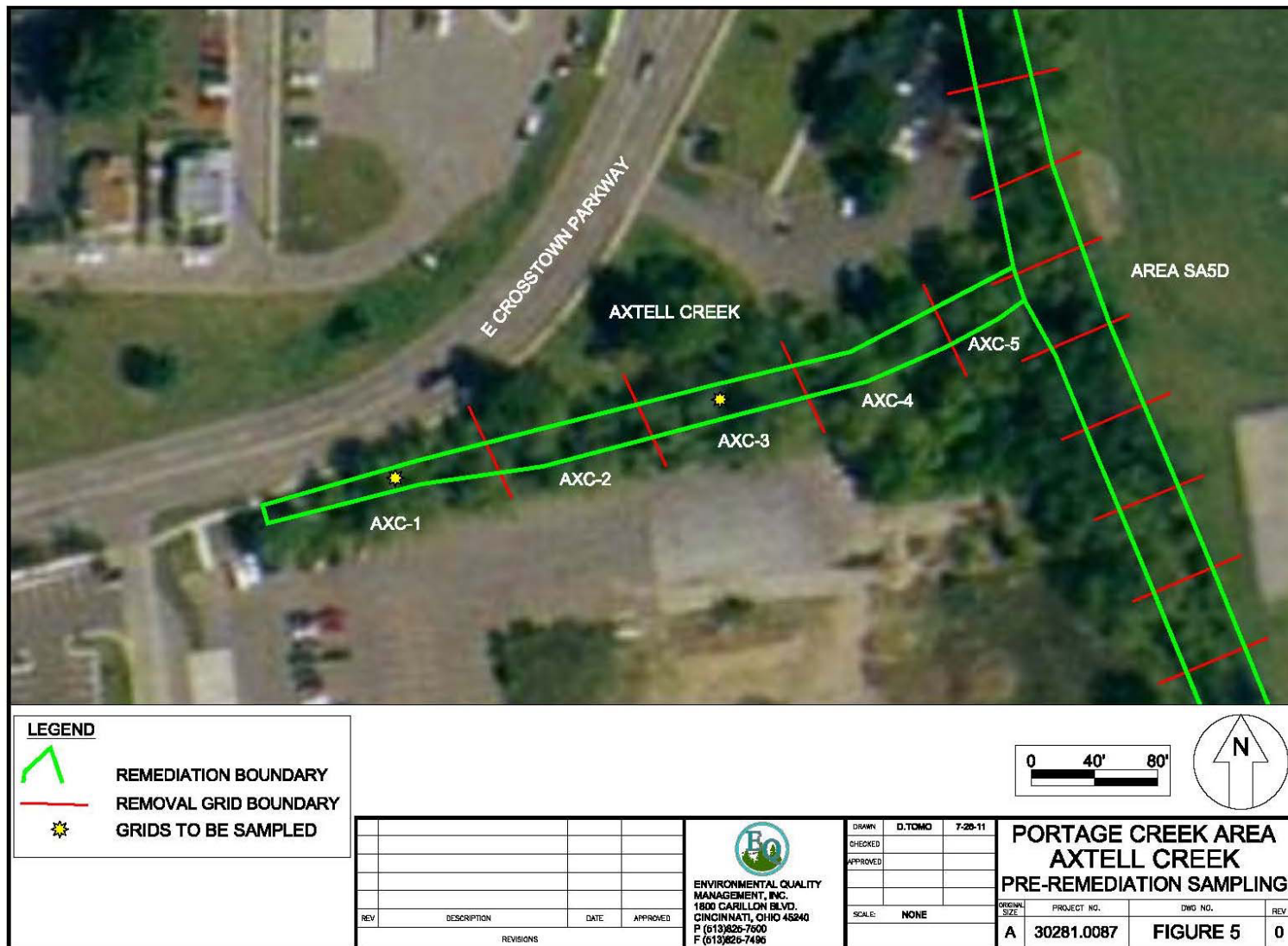


Figure 5. Removal Area Axtell Creek

3281-87PCA.1



Figure 6. Removal Area SA5D

3281-87PCA.1

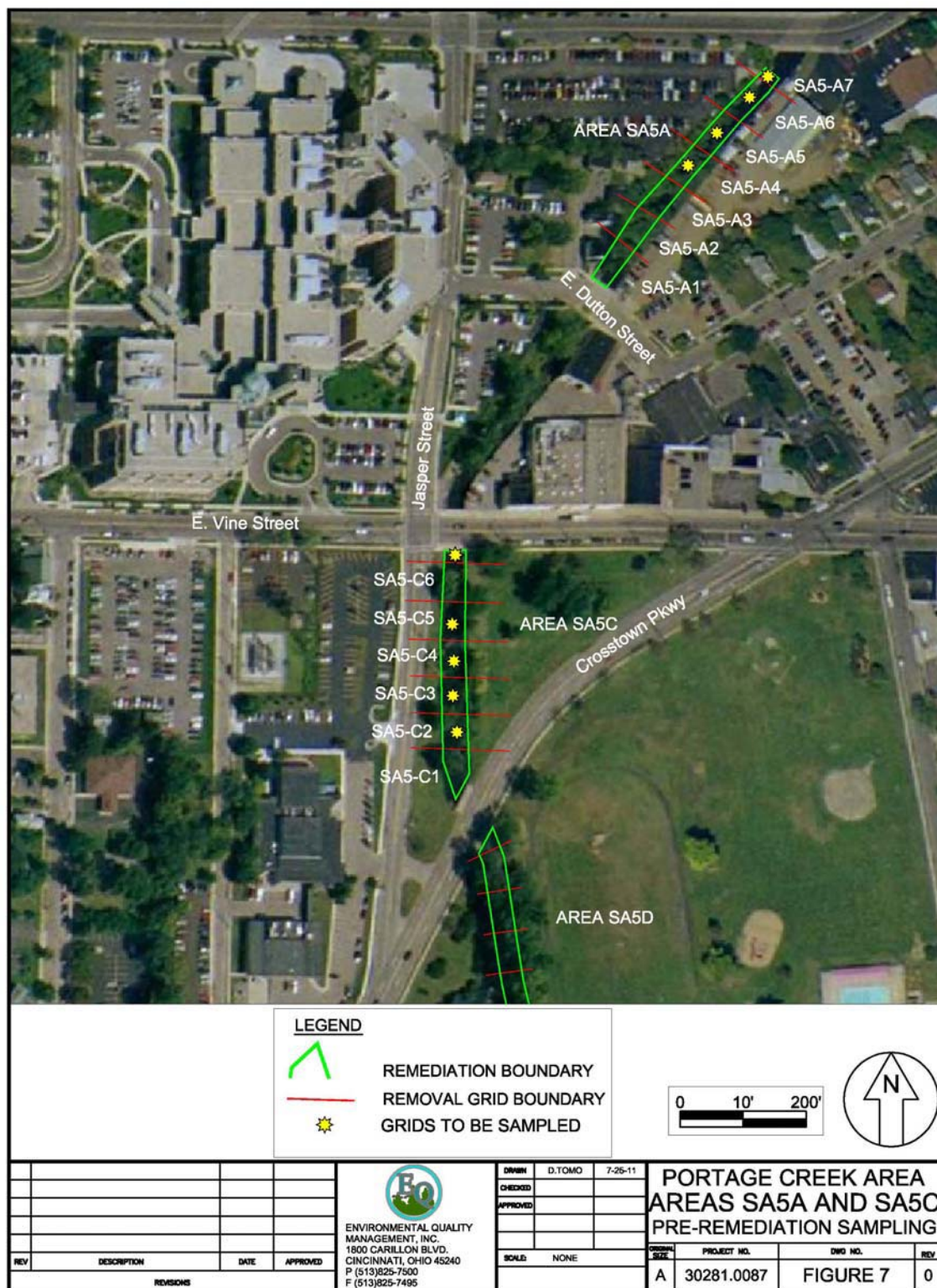


Figure 7. Removal Areas SA5A and SA5C

3281-87PCA.1

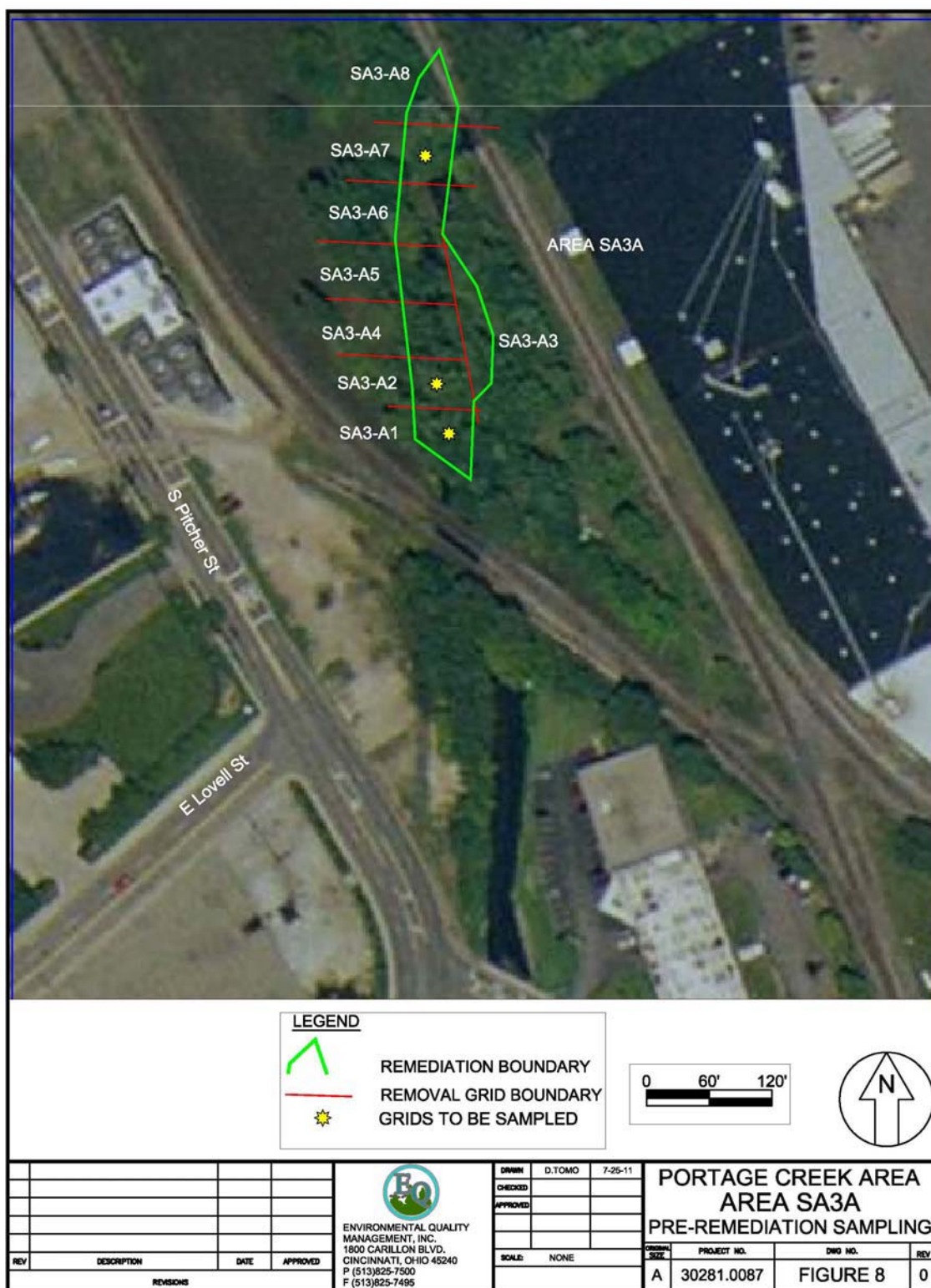


Figure 8. Removal Area SA3

3281-87PCA.1



Figure 9. Removal Area SA1

3281-87PCA.1

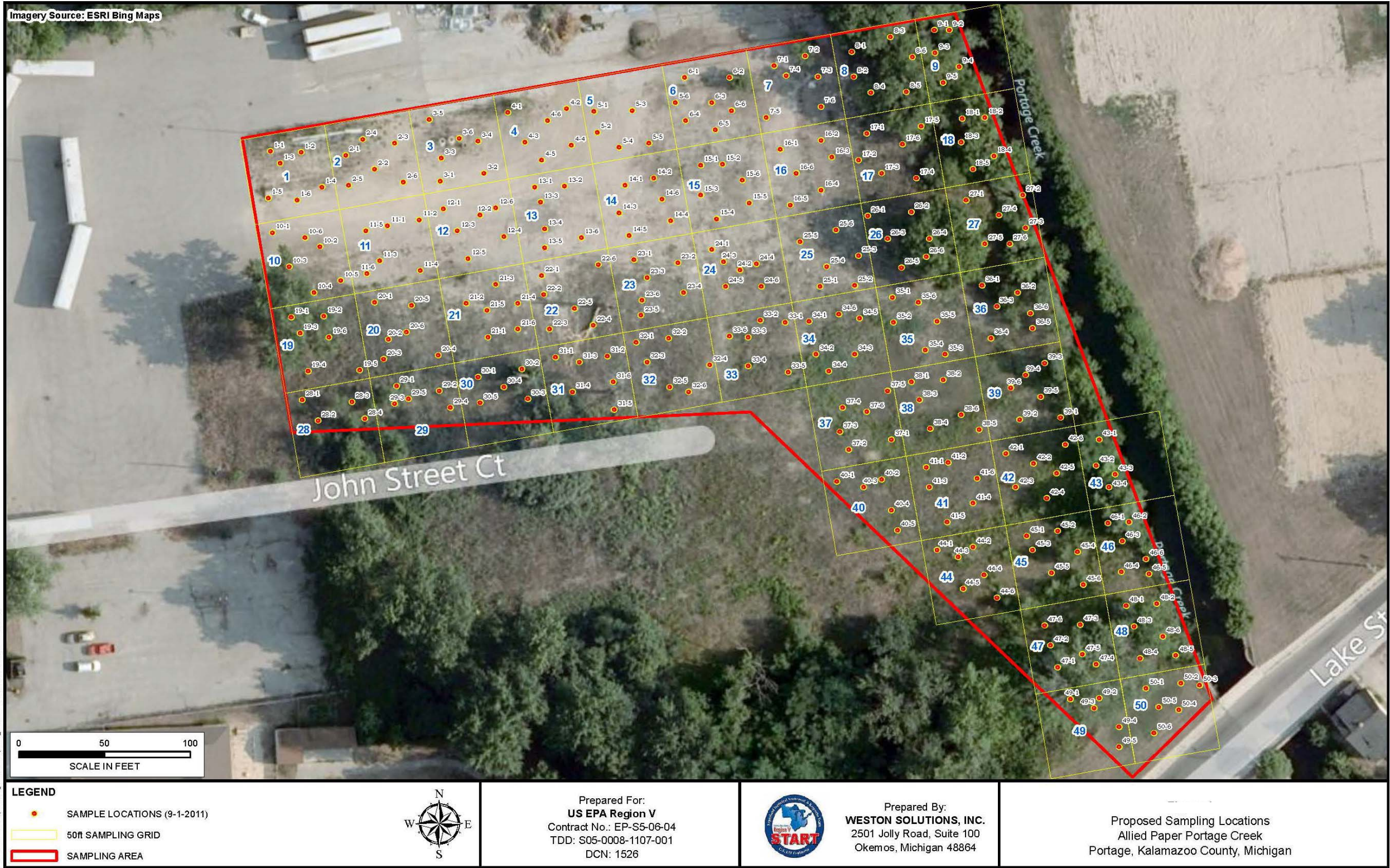


Figure 10. Sampling Locations at the Main Support Area

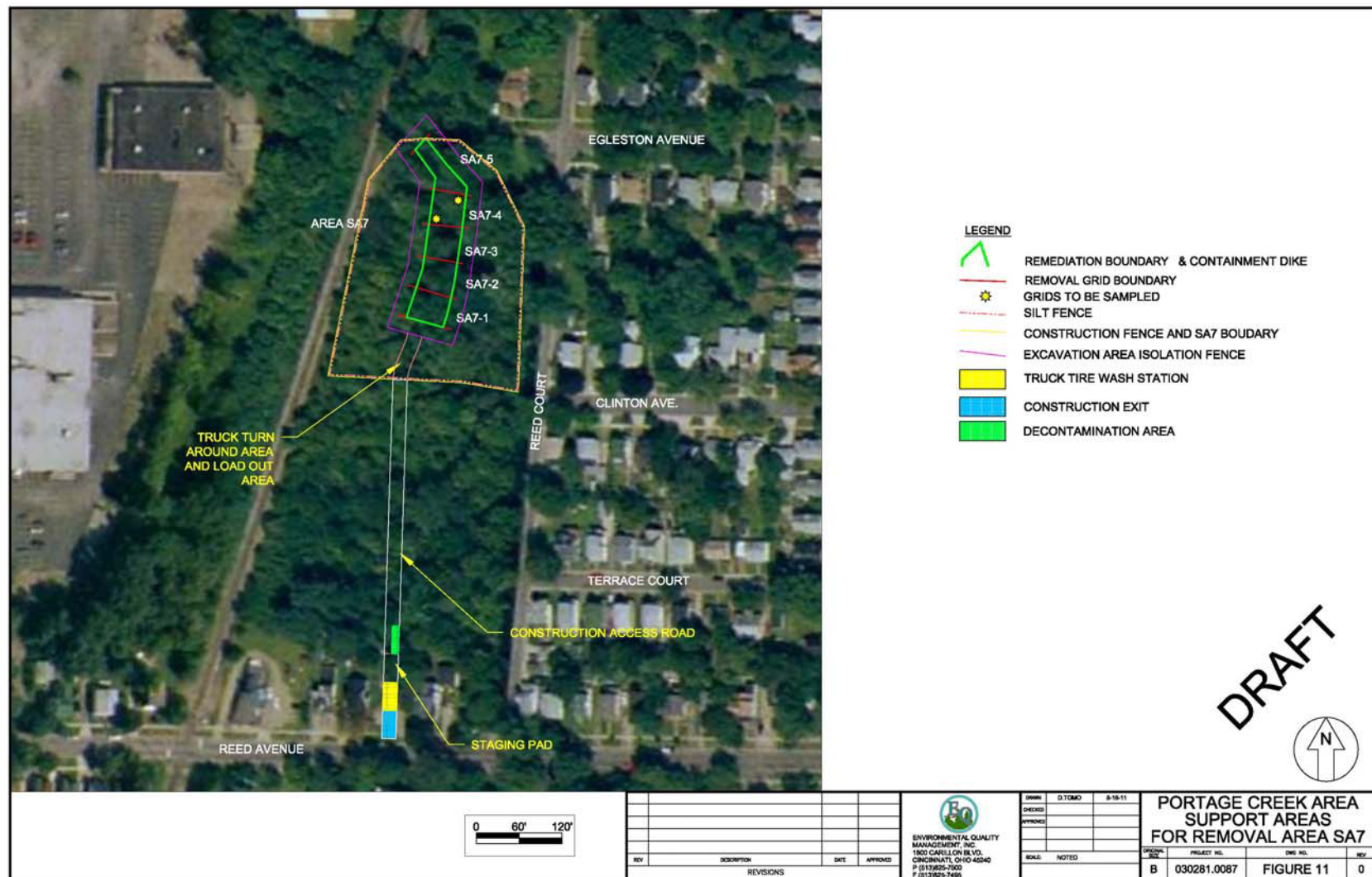


Figure 11. Support Areas for Removal Area SA7

3281-87PCA.1

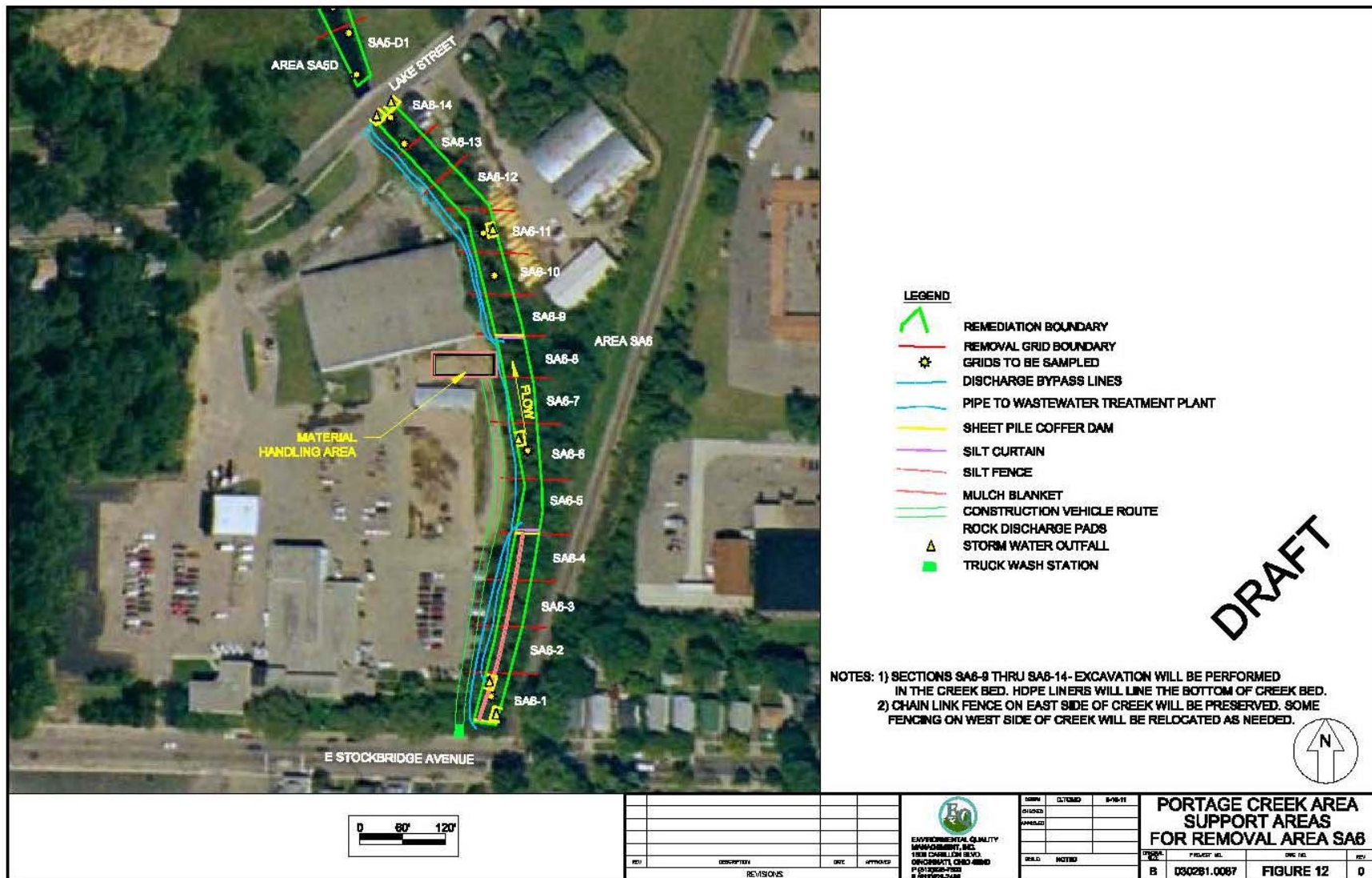


Figure 12. Support Areas for Removal Area SA6

3281-87PCA.1

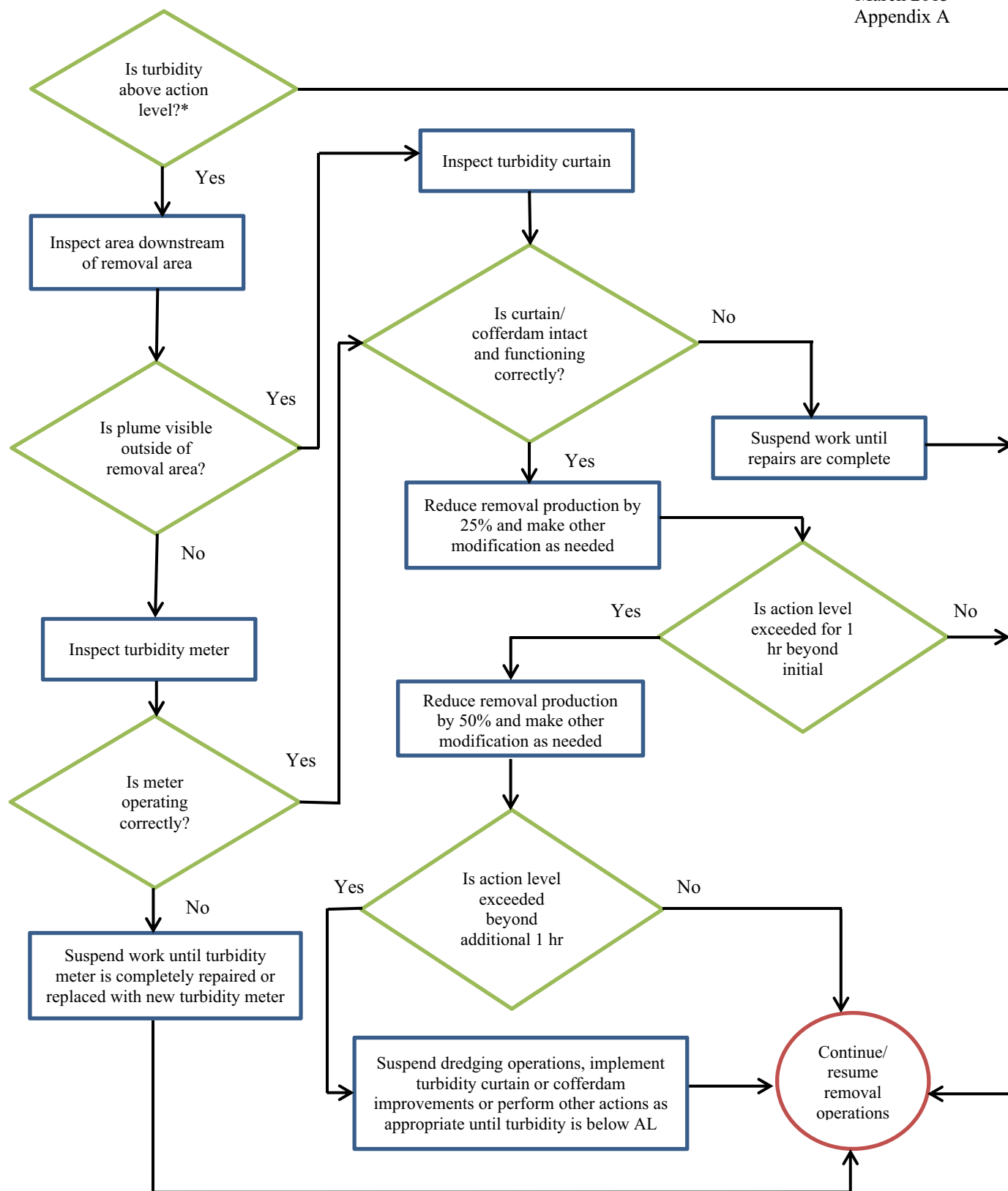


Figure 13. Mitigation Measures Flow Chart for Turbidity Monitoring

3281-87PCA.1

[illegible]

Figure 14. Boring Log

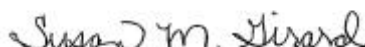
APPENDIX B
ANALYTICAL SOPS

**Title: INDUCTIVELY COUPLED PLASMA – ATOMIC EMISSION
SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE ELEMENT
ANALYSES**

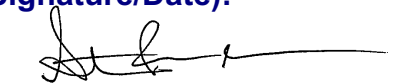
****This revision is NOT applicable for Ohio VAP projects****

[Methods: SW846 Methods 6010B, 6010C, and EPA Method 200.7]

Approvals (Signature/Date):


Technology Specialist

03/30/12
Date


Health & Safety Coordinator

04/02/12
Date


Quality Assurance Manager

04/13/12
Date


Laboratory Director

04/16/12
Date


Technical Director

04/09/12
Date

This SOP was previously identified as SOP NC-MT-012, Rev 2, dated 02/22/11

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Distributed To: _____

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION
SPECTROSCOPY, SPECTROMETRIC METHOD FOR TRACE
ELEMENT ANALYSIS, METHOD 6010B AND METHOD 200.7

SOP No. CORP-MT-0001
Revision No. 0
Revision Date: 11-1-95
Page: 2 of 34

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1. SCOPE AND APPLICATION

- 1.1. This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Methods 6010B, 6010C, and EPA Method 200.7. Tables I and IA of Appendix A lists the elements appropriate for analysis by Methods, 6010B, 6010C, and 200.7 plus the associated reporting limit. Additional elements may be analyzed under Methods, 6010B, 6010C, and 200.7 provided that the method performance criteria presented in Section 13.0 are met.
- 1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity, and optimum concentration ranges of the metals will vary with the matrices and instrumentation used.
- 1.3. Methods 6010B and 6010C are applicable to the determination of dissolved, suspended, total recoverable, and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, biological, and TCLP, EP, and other leachates/extracts. All matrices require digestion prior to analysis. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.
- 1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis. Silver concentrations must be below 0.1 mg/L in aqueous samples.

2. SUMMARY OF METHOD

- 2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by radio frequency inductively-coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and 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 must also be recognized, and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for

which point selection for background correction is superfluous since whole spectral regions are processed.

- 2.1. Refer to NC-IP-010, Acid Digestion of Soils by SW846 Method 3050B, and NC-IP-011, Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, for details on sample preparation methods.

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version for additional definitions. Refer to Appendix B for a cross reference of method definitions.

4. INTERFERENCES

- 4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:
 - Overlap of a spectral line from another element.
 - Unresolved overlap of molecular band spectra.
 - Background contribution from continuous or recombination phenomena.
 - Stray light from the line emission of high concentration elements.
- 4.1.1. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.
- 4.1.2. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.
- 4.1.3. Physical interferences are generally considered to be effects associated with sample transport, nebulization, and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects) at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. 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, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard, and/or use of a high solids nebulizer can reduce the effect. Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.
- 5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.
- 5.3. 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.			

- 5.3.1. The plasma emits strong UV light and is harmful to vision. **NOTE: AVOID looking directly at the plasma.**
- 5.3.2. The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers must not go near the instrument while in operation.
- 5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Metals digestates can be processed outside of a fume hood. Solvent and waste containers must be kept closed unless transfers are being made.
- 5.5. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.
- 6.2. Radio Frequency Generator
- 6.3. Argon gas supply, welding grade or equivalent
- 6.4. Coolflow or appropriate water cooling device
- 6.5. Peristaltic Pump
- 6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes – ranging from 5 μ L \rightarrow 10 ml
- 6.7. Class A volumetric flasks – range from 50 ml \rightarrow 2000 ml
- 6.8. Autosampler tubes

7. REAGENTS AND STANDARDS

- 7.1 Intermediate standards are purchased as custom multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon or unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the

acceptance criteria described in laboratory-specific SOPs are met. Additional information can be found in SOP NC-QA-017. Standard or spiking concentrations, as well as vendors, are subject to change.

- 7.2 Working calibration, calibration verification solutions, and internal standard solutions must be prepared in a matrix of 5% hydrochloric and 5% nitric acids. Refer to Tables II, III, IV and V (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction, and spiking solutions. Refer to the laboratory Standard Logbook or Reagent Logbook for details on standard or reagent preparation.
- 7.3 Concentrated nitric acid (HNO_3), trace metal grade or better.
- 7.4 Concentrated hydrochloric acid (HCl), trace metal grade or better.
- 7.5 Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Sample holding times for metals are six months from time of collection to the time of analysis.
- 8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron is to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.
- 8.3. Soil samples do not require preservation, but must be stored at $4^\circ\text{C} \pm 2^\circ$ until the time of preparation.
- 8.4. Metals samples that are preserved at the laboratory must be held for 24 hours before digestion.

Note: If the samples are preserved the same day of collection, the 24-hour waiting period is not required

9. QUALITY CONTROL

- 9.1. Initial Demonstration of Capability
 - 9.1.1. Prior to analysis of any analyte using Methods 200.7, 6010B, or 6010C, the following requirements must be met.
 - 9.1.2. Instrument Detection Limit (IDL) - The IDL for each analyte must be determined for each analyte wavelength used for each instrument. The IDL must be determined annually for client-specific projects. For DoD work, refer to SOP NC-QA-016. If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined. The IDL will be determined by multiplying by 3,

the standard deviation obtained from the analysis of a blank solution, with seven consecutive measurements. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples).

- 9.1.3. Instrument Detection Limits (IDLs), Method 6010C – IDLs are useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limit of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation; however, it should be understood that the lower limit of quantitation needs to be verified using the criteria in Section 10.7.
- 9.1.4. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. Refer to TestAmerica North Canton SOP NC-QA-021 and CA-Q-S-006 for details on MDL analysis and criteria.
- 9.1.5. Linear Range Verification (LR) - The linear range must be verified every six months for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample. The standards used to verify the linear range limit must be analyzed during a routine analytical run, and must read within 10% of the expected value.

For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard must be near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10% less than the expected level extrapolated from lower standards. If the instrument is adjusted in any way that may affect the LRs, new dynamic ranges must be determined. The LR data must be documented and kept on file.

- 9.1.6. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, 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 inter-element spectral interference, or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the ICP instrument manual for specific procedures to be used in setting background correction points.
- 9.1.7. Inter-element Corrections (IECs) - ICP inter-element correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be

redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC, then the possibility of contamination must be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., ICP-MS). Published wavelength tables (e.g., MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than \pm the RL as defined in Tables I or IA. For elements with a reporting limit of 10 ug/L or less, the signal must be \pm two times the RL. To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the actual concentration of the "interfering element."

Note: Trace ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the Trace as reflected by the ICSA response. Additional spectral interference is present from easily ionizable elements such as potassium and sodium in axial viewing instruments.

9.1.8. Rinse Time Determination - Rinse times must be determined upon initial set-up of an ICP instrument. To determine the appropriate rinse time for a particular ICP system, the linear range verification standard (see Section 9.1.4) must be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to $<$ RL will define the rinse time for a particular ICP system. For some analytes, it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be re-analyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

9.2. Method Blank (MB) - One method blank must be processed with each preparation batch of up to 20 samples. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank must not contain any analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at, or above, 10 % of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of ten times higher than the

blank contamination level). For Ohio VAP projects, all analytes must be less than the reporting limit with the following exceptions: (a) insufficient sample for re-digestion, (b) expired holding times, or (c) the elements detected in the method blank are non-detect for the associated samples.

- If the analyte is a common laboratory contaminant (copper, iron, lead, or zinc), the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. Such action must be addressed in the project narrative.
- Repreparation and re-analysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).
- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be addressed in the project narrative.
- If the above criteria are not met and re-analysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative.

9.3. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table II (Appendix A). The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- If any analyte is outside established control limits, the system is out of control and corrective action must occur. Unless in-house control limits are established, a control limit of 80 - 120% recovery must be applied for Method 6010B and 6010C. For Method 200.7, control limits of 85-115% must be applied.
- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The LCSD recovery is evaluated using the same control limits as the LCS. The RPD of the LCS and LCSD must be compared to in-house limits.
- In the instance where the LCS recovery is greater than the upper control limit and the sample results are < RL, the data may be reported with qualifiers. Such action must be addressed in the report narrative.
- Corrective action will be repreparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable. For Ohio VAP projects, the LCS/LCSD must meet acceptance criteria. The laboratory may re-analyze an aliquot of the LCS/LCSD to verify the outlier; however, if the LCS/LCSD exhibits the same anomaly upon re-analysis, the sample batch must be redigested or re-extracted and re-analyzed. The exceptions are as follows: (a) insufficient sample for re-extraction/re-digestion, (b)

expired holding times, or (c) the LCS is biased high and the samples are non-detect for those analytes.

- 9.4 Additional information on QC samples can be found in QA Policy QA-003. Ohio VAP projects must reference this SOP instead of policy QA-003 for information on QC samples.
- 9.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of, or in addition to, MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Tables II and V (Appendix A).
- If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. For Methods 6010B and 6010C, control limits of 75-125% (70-130% for Method 200.7) recovery and 20% RPD or historical acceptance criteria must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include re-preparation and re-analysis of the sample and MS/MSD. MS/MSD results, which fall outside the control limits, must be addressed in the narrative.
 - If the native analyte concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data is reported with a "4" flag.
 -
 - For Method 6010C samples – If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise, another sample from the same preparation batch should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and must be recovered to within 80% to 120% of the known value. If this spike fails, then the dilution test must be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.
- 9.6 Dilution test – A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5X dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted sample after correction for dilution must agree within 10% of the original sample determination when the original sample concentration is greater than 50 times the MDL. If the results are not within 10%, the possibility of chemical or physical interference exists and the data is flagged.

9.7 Control Limits

9.7.1 Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2 Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMS (QC Browser program).

9.8 Method Detection Limits (MDLs) and MDL Checks

9.8.1 MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.8.2 MDLs are easily accessible via LIMS.

9.9 Nonconformance and Corrective Action

9.9.1 Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action approved by the facility QA Manager. Deviations are not allowed for Ohio VAP projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the instructions in Appendix F.

10.3 Initial Calibration - Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures. Flush the system with the calibration blank between each standard or as the manufacturer recommends. The calibration curve must consist of a minimum of a blank and a standard. Refer to Appendix F for detailed setup and operation protocols. Refer to Instruction Manuals in laboratory. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument standardization date and time must be included in the raw data

10.4 Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV) immediately after the initial calibration. For analyses conducted under Method 200.7, the ICV result must fall within 5% of the true value for that solution with relative standard deviation <3% from replicate (minimum of two) exposures. For Methods 6010B and 6010C, the ICV must fall within $\pm 10\%$ of the true value for that solution. For Method 6010B, the relative standard deviation must be <5% from replicate (minimum of two) exposures. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The calibration blank is prepared with reagent water to the same concentrations of the acids found in the standards. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations. The ICB

result must fall within \pm the RL from zero. If either the ICV or ICB fail to meet criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified (see Sections 11.6 through 11.8 for required run sequence).

- 10.5 Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the sample run. The CCV is to be a mid-range standard made from a dilution of the calibration standard. The CCV for all methods must fall within 10% of the true value for that solution. For Methods 6010B and 200.7, the relative standard deviation must be $<5\%$ from replicate (minimum of two) exposures. For Method 6010C, there is no criteria for RSD from replicate exposures. A CCB is analyzed immediately following each CCV (see Sections 11.6 through 11.8 for required run sequence). The calibration blank is prepared with reagent water to the same concentrations of the acids found in the standards. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations. The CCB result must fall within \pm RL from zero. If the blank is less than 1/10 the concentration of the action level of interest and no sample is within 10% of the action limit, re-analysis and recalibration are not required before continuation of the run. This is not acceptable for Ohio VAP samples. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, all affected samples must be re-analyzed with valid CCV/CCB pairs (refer to Section 11.7 for an illustration of the appropriate rerun sequence). Exceptions: If CCB $>$ RL, samples $<$ RL can be reported with an NCM. If CCV is outside of criteria on the high side, samples $<$ RL can be reported with an NCM.
- 10.6 Interference Check Analysis (ICSA/ICSAB) - The validity of the inter-element correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table IV (Appendix A) for the details of ICSA and ICSAB composition. Custom multi-element ICS solutions must be used. All analytes must be spiked into the ICSAB solution; therefore, if a non-routine analyte is required, then it must be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. If the ICP will display overcorrection as a negative number, then the non-routine elements can be controlled from the ICSA. Elements known to be interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium, and magnesium must always be included in all ICP runs.
- 10.6.1 The ICSA and ICSAB solutions must be run at the beginning of the run (see Sections 11.6 or 11.7 for required run sequence).
- 10.6.2 The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the samples rerun.
- 10.6.3 ICSA results for the non-interfering elements with reporting limits ≤ 10 $\mu\text{g/L}$ must fall within ± 2 times the RL from zero. ICSA results for the non-interfering elements with RLs > 10 $\mu\text{g/L}$ must fall within ± 1 times the RL from zero. If the ICSA results for the non-interfering elements do not fall within \pm two times RL (RL ≤ 10) or $\pm 1 \times \text{RL}$

(RL>10) from zero, the field sample data must be evaluated as follows.

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.
- If the affected element was not required, then the sample data can be accepted.
- If the interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result greater than \pm two times the RL from zero, then the field sample data can be accepted.
- If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than \pm two times the RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than ten times the analyte signal in the ICSA.
- If the data does not meet the above conditions, then the IECs must be re-evaluated and corrected if necessary and the affected samples re-analyzed or the sample results manually corrected through application of the new IEC to the raw results. If the results are recalculated manually, the calculations must be clearly documented on the raw data.

10.7 CRI (CRA or LLICV/LLCCV (6010C) - To verify linearity near the RL for ICP analysis, a CRI standard is run at the beginning of each sample analysis run. Additionally, some projects may require CRI analysis at the end of the run (see Sections 11.6 or 11.7 for required run sequence). Evaluate associated samples based upon advisory limits of \pm 50% of true value. For Method 6010C, it must be analyzed at the beginning and end of the analytical run. The control limit for this method is 70-130%.

Note: The custom CRI mix contains most analytes at a level near the standard lab reporting limit.

11. PROCEDURE

- 11.1. A minimum of two exposures for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.
- 11.2. Prior to calibration and between each sample/standard, the system is rinsed with the calibration blank solution.
- 11.3. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV,CCV), blanks (ICB,CCB,PB), interference checks (ICSA,ICSAB), and field samples (linear range) to improve the data review process.
- 11.4. To facilitate the early identification of QC failures and samples requiring rerun, it is strongly

recommended that sample data be reviewed periodically throughout the run.

11.5. The following procedural guidelines must be followed when using an internal standard:

11.5.1 Typically used internal standard is: yttrium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

11.5.2 The internal standard (IS) must be added to every sample and standard at the same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing coil. Internal standards must be added to blanks, samples, and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

11.5.3 The concentration of the internal standard must be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

11.5.4 The internal standard raw intensity counts must be printed on the raw data.

11.5.5 The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte). The instrument automatically adjusts sample results based on comparison of the internal standard intensity in the sample to the internal standard intensity at calibration.

11.5.5.1 If the internal standard counts fall within $\pm 30\%$ of the counts observed in the ICB or calibration blank then the data is acceptable.

11.5.5.2 If the internal standard counts in the field samples are more than $\pm 30\%$ higher than the expected level, a dilution is needed due to matrix interference.

11.6 The following analytical sequence must be used for Methods 6010B, 6010C, and 200.7:

Instrument Calibration

ICV

ICB

CRI/LLICV (6010C)

ICSA

ICSAB

CCV

CCB

10 samples

CCV

CCB

10 samples

CCV

CCB

Repeat sequence of up to 10 samples between CCV/CCB pairs as required to complete run

CRI (The CRI counts as a sample analysis.) /LLICV (6010C)

CCV

CCB

Refer to Quality Control Section 9.0 for Methods 6010B, 6010C, and 200.7 quality control criteria.

- 11.7 The following run sequence provides an illustration of a mid-run CCV or CCB failure and the appropriate corrective action run sequence as described in Section 10.5.

Original Run: Instrument Calibration

ICV

ICB

CRI

ICSA

ICSAB

CCV

CCB

10 samples

CCV

CCB

10 samples

CCV

CCB

10 samples **

CCV *

* Failure occurs at CCV/CCB

CCB *

**Samples requiring rerun for affected analytes

10 samples **

CCV

CCB

10 samples

CCV

CCB

- 11.8 The instrument may be reprofiled between CCV/CCB pairs to correct for environment-induced drift.
- 11.9 Guidelines are provided in the Appendix C, D, and E on procedures to minimize contamination of samples and standards, preventive maintenance, and troubleshooting.
- 11.10 All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that

exceed the linear range. If an inter-element correction exists for an analyte, which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an overrange analyte may not be required to be reported for a sample, if that analyte is an interferent for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

- 11.11 Any variation in procedure must be completely documented using instrument run logs, maintenance logs, report narratives, a Nonconformance Memo, or an anomaly report; and is approved by a Supervisor/Group Leader and QA Manager.
- 11.12 Nonconformance documentation must be filed in the project file.
- 11.14 Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.
- 11.15 Analytical Documentation
 - 11.15.1 Record all analytical information LIMS, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.
 - 11.15.2 All standards are logged into the LIMS standard and reagent module. All standards are assigned a unique number for identification.
 - 11.15.3 Documentation, such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs, is available for each data file.
 - 11.15.4 Sample results and associated QC are entered into LIMs where they will under-go a level 1 and level 2 technical review.

12 DATA ANALYSIS AND CALCULATIONS

- 12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(ICV)}{True(ICV)} \right)$$

- 12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(CCV)}{True(CCV)} \right)$$

- 12.3. Matrix Spike Recoveries are calculated according to the following equation:

$$\% R = 100 \left(\frac{SSR - SR}{SA} \right)$$

Where:

SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

- 12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equations:

$$RPD = 100 \left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2} \right)} \right]$$

Where:

MS = determined spiked sample concentration

MSD = determined matrix spike duplicate concentration

- 12.5. The final concentration for a digested aqueous sample is calculated as follows:

$$mg / L = \frac{C \times V1 \times D}{V2}$$

Where:

C = Concentration (mg/L) from instrument readout (mean of two exposures)

D = Instrument dilution factor

V1 = Final volume in liters after sample preparation

V2 = Initial volume of sample digested in liters

- 12.6. The final concentration determined in digested solid samples is calculated as follows:

$$mg / Kg, dry weight = \frac{C \times V \times D}{W}$$

Where:

C = Concentration (mg/L) from instrument readout (mean of two exposures)

D = Instrument dilution factor

V = Final volume in liters after sample preparation

W = Weight in Kg of wet sample digested

- 12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100 \left(\frac{Found(LCS)}{True(LCS)} \right)$$

12.8. The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:

I = Sample result (Instrument reading)

S = Dilution test result (Instrument reading \times 5)

12.9. Appropriate factors must be applied to sample values if dilutions are performed.

12.10. Trivalent Chromium

12.10.1 Trivalent chromium (Cr^{+3}) is the result obtained by subtracting the hexavalent chromium (Cr^{+6}) results for a sample from the total chromium result from that sample. The total chromium result is determined using the procedures in this SOP. The hexavalent chromium result is determined using the procedures in TestAmerica North Canton SOP NC-WC-024.

12.10.2 Reporting Limits

12.10.1 The TestAmerica North Canton water reporting limit for trivalent chromium is 0.02 mg/l.

12.10.2 The TestAmerica North Canton solid reporting limit for trivalent chromium is 2.0 mg/kg, wet weight.

12.10.3 Calculations: $Cr^{+3} = Cr, \text{ total} - Cr^{+6}$

12.10.3 Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Refer to Tables I and IA in Appendix A for the list of analytes that may be analyzed using this SOP.

13.3. Training Qualification

- 13.3.1 The Group/Team Leader or the Supervisor has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

- 14.1 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".

15. WASTE MANAGEMENT

- 15.1. All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."
- 15.2. Waste Streams Produced by this Method
- 15.2.1. The following waste streams are produced when this method is carried out:
- 15.2.2. Acid waste consisting of sample and rinse solution. Any sample waste generated must be collected and disposed of in the acid waste drum located in the Metals Lab.
- 15.2.3. Standards must be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

- 16.1. References
- 16.1.1. 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits
- 16.1.2. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Revision 2, December 1996. Method 6010B
- 16.1.3. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Final Update IV, Method 6010C, Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 3, February 2007

- 16.1.4. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7
- 16.1.5. Inductively Coupled Plasma – Atomic Emission Spectrometric Method for Trace Element Analysis of water and wastes Method 200.7, 40 CFR – Chapter I – Part 136 – Appendix C. Electronic version dated September 30, 2002
- 16.1.6. [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version
- 16.1.7. TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version
- 16.1.8. [Corporate Quality Management Plan \(CQMP\)](#), current version
- 16.1.9. Revision History

Historical File:		Revision 2.0: 10/27/97		Revision 0: 01/08/04 (NC-MT-012)
(formerly CORP-MT-0001NC)		Revision 2.1: 04/19/99		Revision 1: 01/07/09
		Revision 3.1: 10/04/00		Revision 2: 02/22/11
		Revision 3.2: 01/19/01		
		Revision 3.3: 12/05/01		
		Revision 3.4: 01/08/04		

16.2. Associated SOPs and Policies, current version

- 16.2.1. TestAmerica North Canton QC Program, [QA-003](#)
- 16.2.2. Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)
- 16.2.3. Method Detection Limits and Instrument Detection Limits, [NC-QA-021](#) and [CA-Q-S-006](#)
- 16.2.4. Supplemental Practices for DoD Project Work, [NC-QA-016](#)
- 16.2.5. Hexavalent Chromium (Colorimetric), [NC-WC-024](#)
- 16.2.6. Acid Digestion of Soils, SW846 Method 3050B, [NC-IP-010](#)
- 16.2.7. Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, [NC-IP-011](#)

16.2.8. Standards and Reagents, [NC-QA-017](#)

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method

17.1.1. Modifications/interpretations from Methods 6010B and 200.7

- 17.1.1.1. TestAmerica North Canton Laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in-house as recommended by the subject methods.
- 17.1.1.2. Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution must fall within a specific concentration range around the calibration blank. In determining IECs because of lack of definition clarification for “concentration range around the calibration blank,” TestAmerica North Canton has adopted the procedure in EPA CLP ILMO4.0.
- 17.1.1.3. Whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because TestAmerica North Canton laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, TestAmerica North Canton may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At TestAmerica North Canton, matrix interference is determined by evaluating data for the LCS and MS/MSD. TestAmerica North Canton REQUIRES documented, clear guidance when a new or unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.1.2. Modifications from Method 200.7

- 17.1.2.1. Method 200.7 defines the IDL as the concentration equivalent to a signal due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength. TestAmerica North Canton labs utilize the IDL definition as defined in Section 9.1 of this SOP.
- 17.1.2.2. The calibration blank is prepared in an acid matrix of 5% HNO₃/5% HCl instead of the specified 2% HNO₃/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols

applied.

- 17.1.2.3. Method Section 9.3.4 specifies that “Analysis of the ICV (ICSA/AB) solution immediately following calibration must verify that the instrument is within $\pm 5\%$ of calibration with a relative standard deviation $<3\%$ from replicate integrations ≥ 4 ”. TestAmerica North Canton uses a minimum of two exposures.
 - 17.1.2.4. The 40 CFR version of Method 200.7 requires the instrument check standard to agree within $\pm 5\%$ of expected values and less than, or equal to, 3% RSD. Also, the 40 CFR version requires the interference check sample to be analyzed at the beginning, end, and at periodic intervals throughout the sample run. At TestAmerica North Canton, the instrument check standard equals the CCV, which must agree within $\pm 10\%$ of expected values and 5% RSD, and the ICSA standards are analyzed only at the beginning of a sample run. TestAmerica’s procedures are in line with the Rev. 4.4, May 1994 version of Method 200.7.
 - 17.1.2.5. Section 7.12 of Method 200.7 indicates that the QCS (ICV) must be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.
 - 17.1.2.6. The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 Section 10.4 states that results must fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. The control limits listed in this SOP are those applicable to the EPA designed solution.
 - 17.1.2.7. Method 200.7 Section 9.3.4 states the CCB must be less than the IDL, but more than the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica North Canton has adopted an absolute control limit of \pm RL from zero for calibration blank criteria. SOP Section 10.5 provides the detailed corrective action criteria that must be followed.
- 17.1.3. Modifications from Method 6010B
- 17.1.3.1. Chapter 1 of SW-846 states that the method blank must not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client. This is not

acceptable for Ohio VAP projects.

- 17.1.3.2. Method 6010B Section 8.6.1.3 states that the results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two or more times, and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and re-analyze the previous ten samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica North Canton has adopted an absolute control limit of \pm RL from zero for calibration blank criteria. See SOP Section 10.5 for a detailed description of the required corrective action procedures.

APPENDIX A - TABLES

TABLE I: Methods 200.7, 6010B, and 6010C Target Analyte List

Element	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	200	20
Antimony	Sb	7440-36-0	60	6
Arsenic	As	7440-38-2	300	30
Barium	Ba	7440-39-3	200	20
Beryllium	Be	7440-41-7	5.0	0.5
Boron	B	7440-42-8	200	20
Cadmium	Cd	7440-43-9	5.0	0.5
Calcium	Ca	7440-70-2	5000	500
Chromium	Cr	7440-47-3	10	1
Cobalt	Co	7440-48-4	50	5
Copper	Cu	7440-50-8	25	2.5
Iron	Fe	7439-89-6	100	10
Lead	Pb	7439-92-1	100	10
Magnesium	Mg	7439-95-4	5000	500
Manganese	Mn	7439-96-5	15	1.5
Molybdenum	Mo	7439-98-7	40 (100 for 200.7)	4
Nickel	Ni	7440-02-0	40	4
Potassium	K	7440-09-7	5000	500
Selenium	Se	7782-49-2	250	25
Silver	Ag	7440-22-4	10	1
Sodium	Na	7440-23-5	5000	500
Thallium	Tl	7440-28-0	2000	200
Vanadium	V	7440-62-2	50	5
Zinc	Zn	7440-66-6	20 (50 for 200.7)	2
Tin	Sn	7440-31-5	100	10
Titanium	Ti	7440-32-6	50	5

TABLE IA: Methods 200.7, 6010B, and 6010C Trace ICP Target Analyte List

Element	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil
Arsenic	As	7440-38-2	10	1.0
Lead	Pb	7439-92-1	3.0	0.3
Selenium	Se	7782-49-2	5.0	0.5
Thallium	Tl	7440-28-0	10	1.0
Antimony	Sb	7440-36-0	10	1.0
Cadmium	Cd	7440-43-9	2.0	0.2
Silver	Ag	7440-22-4	5.0	0.5
Chromium	Cr	7440-47-3	5.0	0.5
Cobalt	Co	7440-48-4	7.0	5.0
Titanium	Ti	7440-32-6	50	5.0
Vanadium	V	7440-62-2	7.0	5.0
Molybdenum	Mo	7439-98-7	10	1.0

TABLE II: Matrix Spike and Aqueous Laboratory Control Sample Levels

Element	Concentration (ug/L)
Aluminum	2000
Antimony	500
Arsenic	2000
Barium	2000
Beryllium	50
Cadmium	50
Calcium	50000
Chromium	200
Cobalt	500
Copper	250
Iron	1000
Lead	500
Magnesium	50000
Manganese	500
Molybdenum	1000
Nickel	500
Potassium	50000
Selenium	2000
Silver	50
Sodium	50000
Thallium	2000
Vanadium	500
Zinc	500
Boron	1000
Tin	2000
Titanium	1000

TABLE III: Trace ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	50000	200	12500	25000
Antimony	1000	10	250	500
Arsenic	1000	10	250	500
Barium	4000	10	1000	2000
Beryllium	4000	5	1000	2000
Cadmium	1000	2	250	500
Calcium	100000	5000	25000	50000
Chromium	4000	5	1000	2000
Cobalt	4000	50	1000	2000
Copper	4000	25	1000	2000
Iron	50000	100	12500	25000
Lead	1000	3	250	500
Magnesium	100000	5000	25000	50000
Manganese	4000	15	1000	2000
Molybdenum	4000	40	1000	2000
Nickel	4000	40	1000	2000
Potassium	100000	5000	25000	50000
Selenium	1000	5	250	500
Silver	2000	5	500	1000
Sodium	100000	5000	25000	50000
Thallium	2000	10	500	1000
Vanadium	4000	50	1000	2000
Zinc	4000	20	1000	2000
Boron	10000	200	1000	5000
Tin	10000	100	1000	5000
Titanium	10000	50	1000	5000

TABLE IV: Interference Check Sample Concentrations

Element	ICSA (ug/L)	ICSAB (ug/L)
Aluminum	500000	500000
Antimony	-	1000
Arsenic	-	1000
Barium	-	500
Beryllium	-	500
Cadmium	-	1000
Calcium	500000	500000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200000	200000
Lead	-	1000
Magnesium	500000	500000
Manganese	-	500
Molybdenum	-	1000
Nickel	-	1000
Potassium	-	10000
Selenium	-	1000
Silver	-	1000
Sodium	-	10000
Thallium	-	1000
Vanadium	-	500
Zinc	-	1000
Tin	-	1000
Boron		1000
Titanium		1000

TABLE V: TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

Element	Reporting Level (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

**APPENDIX B - CROSS REFERENCE OF TERMS COMMONLY USED IN
METHODS EPA 200.7, SW 6010B, 6010C, AND
TESTAMERICA NORTH CANTON SOP**

EPA 200.7	SW 6010B / 6010C	TestAmerica North Canton SOP
Calibration blank (CB)	Calibration blank	Initial and continuing calibration blanks (ICB/CCB)
Dilution test	Dilution test	Dilution Test
Instrument detection limit (IDL)	Instrument detection limit (IDL)	Instrument detection limit (IDL)
Instrument performance check (IPC)	Continuing calibration verification (CCV)	Continuing calibration verification (CCV)
Internal standard	Internal standard	Internal standard (IS)
Laboratory duplicates	N/A	N/A
Laboratory fortified blank (LFB)	N/A	Laboratory control sample (LCS)
Laboratory fortified sample matrix (LFM)	Matrix spike and matrix spike duplicate (MS/MSD)	Matrix spike and matrix spike duplicate (MS/MSD)
Laboratory reagent blank (LRB)	Method blank	Method or Prep blank (MB)
Linear dynamic range (LDR)	Linear dynamic range (LDR)	Linear dynamic range (LDR)
Method detection limit (MDL)	Method detection limit (MDL)	Method detection limit (MDL)
Quality control sample (QCS)	Check standard or Initial calibration verification (ICV)	Initial calibration verification (ICV)
Spectral interference check solution (SIC)	Interference check solution (ICS)	Interference check solution (ICSA/ICSAB)

APPENDIX C - TROUBLESHOOTING GUIDE

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber
Instrument Drift	Replace torch (Crack) Clean or replace nebulizer (blockage) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Reprofile
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage (back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

APPENDIX D - CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware must be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the Metals Lab. All work areas must be kept scrupulously clean.

Powdered Gloves must not be used in the Metals Lab since the powder contains silica and zinc as well as other metallic analytes. Glassware must be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipette tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

APPENDIX E - PREVENTATIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs, indicate the date, time and instrument number. Then identify the problem and corrective action in the Maintenance Log.

The following procedures are required to ensure that that the instrument is fully operational:

Change sample pump tubing and pump windings

As Needed: Check rinse solution and fill if needed
Check waste containers and empty if needed
Check sample capillary tubing is clean and in good condition
Check droplet size to verify nebulizer is not clogged.
Check sample flow for cross flow nebulizer
Check pressure for vacuum systems
Clean plasma torch assembly to remove accumulated deposits
Clean nebulizer and drain chamber; keep free-flowing to maintain optimum performance
Replace peristaltic pump tubing, sample capillary tubing and autosampler sipper probe
Apply silicon spray on autosampler tracks
Check water level in cool flow
Change oil for vacuum systems
Replace coolant water filter (may require more or less frequently depending on quality of cooling water)

APPENDIX F - ICP Operating Instructions

ICP Analysis (TJA 61E) Example

1. SETUP

- a. Plasma Control Panel (enter)
- b. (F1) - Startup
- c. (F9) - Continue
- d. (F2) - Levels
 1. Change auxiliary gas to low – use space bar to toggle
 2. Change nebulizer gas flow to 0.5 L/min.
 3. Change pump rate to 130
 4. Escape
 5. Allow instrument to warm up approximately 30 minutes.

2. DEVELOPMENT

- a. Methods (enter)
- b. Enter method name
- c. (F3)-Method Info.
- d. Change file name
- e. (F9) - Done
- f. (F9) - Done/Keep

3. OPERATION

- a. Analysis (enter)
- b. (F5)-Profile
 1. (F3) - Automatic
 2. (F1) - Run
 3. If peak position is greater than ± 0.05 units from the center peak position, you must adjust the profile. If it is within ± 0.05 units, press (F9) - Done.
 4. To adjust select (F1) - CalcSS and enter current vernier position. (enter)
 5. Adjust to new vernier position (F9) - Done
 6. Rerun profile until peak position is ± 0.05 units.
 7. (F9) - Done
- c. Autosampler (F9)
 1. Enter method name (enter)
 2. Enter autosampler table name (enter)
 3. (F1) - Run

Title: INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY

This revision is not applicable for Ohio VAP projects

[Method: EPA Method 200.8, SW846 Methods 6020 and 6020A]

Approvals (Signature/Date):


Technology Specialist 04/25/12
Date


Health & Safety Coordinator 04/26/12
Date


Quality Assurance Manager 04/26/12
Date


Laboratory Director 04/26/12
Date

This SOP was previously identified as SOP No. NC-MT-002, Rev 4.6, dated 02/15/11

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1. SCOPE AND APPLICATION

- 1.1. This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on SW-846 protocol as described in EPA Methods 6020, 6020A, and 200.8. The source method lists the following elements approved for analysis by ICP/MS (Al, Sb, As, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Tl, Se, Na, V, and Zn). Additional elements may be included provided that the method performance criteria presented in Section 9 is met. However, project approval may be required from the controlling agencies for compliance testing beyond the elements included in the method. Reporting limits are listed in Table VI.
- 1.2. The procedure is applicable to the analysis of waters (groundwaters and surface waters), soils, and wastes. Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, biological matrices, and other solid wastes for which total (acid-leachable) elements are requested. See SOPs NC-IP-010 and NC-IP-011 for preparation details.
- 1.3. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

- 2.1. Aqueous samples, digestates, or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into a radio frequency inductively coupled plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas, and by means of a water-cooled differentially-pumped interface, introduced into a high-vacuum chamber that houses a quadrupole mass spectrometer capable of providing a resolution less than, or equal to, 0.9 AMU full width at 10% of the peak height. For analysis by Method 200.8, the resolution requirement is 1.0 amu at 5% peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier. Interference must be assessed and valid corrections applied, or the data flagged, to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents and the constituents of the sample matrix. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

- 4.1. Isobaric Interferences. Isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software.
- 4.2. Isobaric Molecular and Doubly Charged Ion Interferences. Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied; and the data flagged to indicate the presence of interferences. These interferences can be reduced by using Collision Cell Technology (CCT). Collision Cell Technology is accomplished by adding an auxiliary gas into the lens chamber. A Hydrogen/Helium gas mixture is used. This gas mixture is used to knock polyatomic ions out of the path as they collide with the cell gas. The ions are dissociated into their component atoms/ions or converted into non interfering species. The transmission of analyte ions is minimally affected. This process is called Kinetic Energy Displacement (KED).
- 4.3. Physical Interferences. Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.
 - 4.3.1. Internal standards should be added at a level to give approximately 100,000 – 1,000,000 counts of raw signal intensity. Generally, the mass of the internal standard should be no more than 50 AMU (Atomic Mass Unit) of the mass of the measured analyte.
 - 4.3.2. Matrix effects will be monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank. When performing Method 6020, the internal standard intensities must be between 30% and 120% of the intensities in the calibration blank. When performing Method 6020A, the internal standard intensities must be between 70% and 130% of the intensities in the calibration blank. When performing Method 200.8, the internal standards must be between 60% and 125% of the calibration blank. If they fall outside this window, a dilution is performed on the sample to correct for matrix effects and the sample re-analyzed.
 - 4.3.3. Memory effects are dependent on the relative concentration differences between samples and/or standards, which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

- 4.3.4. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be demonstrated routinely to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.
- 5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.
- 5.3. 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.

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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.4. The RF Generator produces strong radio frequency waves--most of which are unshielded. People with pacemakers must not go near the instrument while in operation.
- 5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.
- 5.6. Standards in solution must be diluted in the open laboratory when syringes and the like are utilized.
- 5.7. The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.
- 5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor and the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

- 6.1. Argon gas: High purity grade (99.99%)
- 6.2. Inductively Coupled Plasma Mass Spectrometer capable of providing resolution less than, or equal to, 1.0 AMU at 10% peak height from a mass range of at least 6-240 and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass flow controller for the nebulizer argon and a peristaltic pump for the sample solution is recommended.

- 6.3. A four channel peristaltic pump
- 6.4. Appropriate water-cooling device
- 6.5. Calibrated automatic pipettes
- 6.6. Autosampler with autosampler tubes
- 6.7. Hydrogen/helium gas mixture with approximate ratio of 7% hydrogen and 93% helium used for CCT mode.

7. REAGENTS AND STANDARDS

- 7.1. Calibration standards are purchased as custom multi-element mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Additional information can be found in SOP NC-QA-017.
- 7.2. Check Calibration Standard (ICV) - A quality control standard similar to the calibration standards and prepared in the same acid matrix. This solution must be made at a concentration near the midpoint of the calibration curve. This standard is composed of analytes from a different source from those used in the calibration of the instrument. See Table V. Refer to the LIMS standards and reagents module for details on preparation.
- 7.3. The tuning solution is purchased as custom multi-element mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. The solution must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year.
- 7.4. Reagent water - ASTM Type I, or equivalent for the elements of interest, generated using an ion-exchange water polishing system.
- 7.5. Rinse Solution - Carefully dilute 80 ml of concentrated HNO₃ to 4.0 L with reagent water.
- 7.6. Concentrated nitric acid (HNO₃), trace metal grade or better.
- 7.7. Concentrated hydrochloric acid (HCl), trace metal grade or better

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1. Aqueous samples are preserved with nitric acid to a pH of < 2 , and may be stored in plastic or glass. Preservation must be verified prior to analysis.
- 8.2. Soil samples do not require preservation, but must be stored at $4^{\circ} \pm 2^{\circ}\text{C}$ until the time of preparation.
- 8.3. The analytical holding times for metals are six months from the time of collection to analysis.
- 8.4. Solid and aqueous samples must be digested prior to analysis by the appropriate method.
- 8.5. Samples preserved in the laboratory must be held for 24 hours before digestion.

Note: If the samples are preserved the same day of collection, the 24-hour waiting period is not required.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

- 9.1.1. Instrument Detection Limit (IDL). IDLs can be determined by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as a separate analytical sample. The IDL must be performed every three months. The IDL is calculated by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days.

9.1.1.1. $\text{IDL} = (3) (s)$, where s = standard deviation.

- 9.1.2. Linear Calibration Ranges - Linear calibration ranges are primarily detector limited. The linear range must be determined at instrument setup, and the upper limit must be verified annually or whenever a change in instrument hardware or operating conditions occurs. In the judgement of the analyst, linear ranges may be lowered based on results obtained during the verification process. Standards used to determine or verify linear ranges must be analyzed during a routine analytical run. The linear range is the concentration above which sample results cannot be reported. The linear range must be verified every six months for Method 6020A.

9.1.2.1. For initial determination of the upper limit of the linear range, determine the signal responses from three different concentration standards across

the estimated range. One standard must be at the upper limit of the estimated range. Results must recover within 10% of the expected value for the three standards. The linear range is then set at the concentration of the high standard.

- 9.1.2.2. For verification of the upper limit of the linear range, the high standard must recover within 10% of its expected value

9.2. Batch Definition

- 9.2.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.3. Method Blank

- 9.3.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank must not contain any analyte of interest at, or above, the reporting limit (exception: common laboratory contaminants, see below) or at, or above, 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 10x higher than the blank contamination level).

Note: For Ohio VAP samples, all analytes must be less than the reporting limit unless the samples are non-detect.

9.3.2. Corrective Action for Method Blank

- 9.3.2.1. If the analyte is a common laboratory contaminant (copper, iron, lead, barium, chromium, manganese, calcium, potassium, magnesium, sodium, or zinc), the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. **Such action must be addressed in the project narrative. This is not applicable for Ohio VAP samples.**

- 9.3.2.2. Repreparation and re-analysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).
- 9.3.2.3. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be addressed in the project narrative.
- 9.3.2.4. If the above criteria are not met and re-analysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative.

9.4. Laboratory Control Sample (LCS)

9.4.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The historical limits for the LCS for each analyte are in the LIMS system. If the LCS exceeds these limits for any analyte, that analyte is judged to be out of control and must be corrected before the analysis can be reported. For Method 200.8, LCS limits are 85-115%.

9.4.2. Corrective Action for LCS

- 9.4.2.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.
- 9.4.2.2. The only exception is if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest. **This must be addressed in the project narrative.**
- 9.4.2.3. Corrective action will be repreparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

Note: For Ohio VAP samples, the batch must be redigested if the exception in Section 9.4.2.2 is not applicable.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked

identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of, or in addition to, MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. The historical spike recovery acceptance limits for each analyte are in the LIMS system. If they are not in control, and all other quality control criteria have been met, then a matrix interference is suspected.

9.5.2. Corrective action for MS/MSDs

- 9.5.2.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control; and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include re-preparation and re-analysis of the sample and MS/MSD.
- 9.5.2.2. If the native analyte concentration in the MS/MSD exceeds four times the spike level for that analyte, the recovery data is flagged with a "4" in LIMS.
- 9.5.2.3. If client program requirements specify to confirm matrix interferences, re-preparation and re-analysis of the MS/MSD may be necessary.
- 9.5.2.4. For Method 6020A, a post digestion spike will be run on a sample if the MS/MSD for the sample falls outside of the % recovery criteria. A post digestion spike is a matrix spike on the same sample from which the MS/MSD aliquots were prepared, where the spike is added after the sample preparation is completed. The post digestion spike recovery for Method 6020A should be within 80-120%. If this spike fails, then the dilution test should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed. A post digestion spike is not required for Method 200.8 nor Method 6020.

9.6. Sample Duplicate

- 9.6.1. A sample duplicate (DU) is a second aliquot of an environmental sample taken from the same sample container, when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent

samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.6.2. Sample duplicates may be performed in lieu of, or in addition to, MSDs.

9.7. Control Limits

9.7.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.7.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMs.

9.8. Method Detection Limits (MDLs) and MDL Checks

9.8.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.8.2. MDLs are easily accessible via LIMs.

9.9. General Corrective Action Requirements. The general requirements for evaluation of QC results and corrective action for failures is described in TestAmerica Policy QA-003. Ohio VAP projects must reference this SOP instead of Policy QA-003 for information on QC Samples.

9.10. Nonconformance and Corrective Action

9.10.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action. Procedural deviations are not allowed for Ohio VAP Projects.

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument Startup. Set up the instrument according to manufacturers operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning.

10.2. Instrument Tuning / Mass Calibration / Daily Performance

10.2.1. Daily Performance. Refer to Appendix A for ICPMS Instrument Instructions. Instrument manuals are available as needed. Verify instrument performance daily with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the

tuning solution a minimum of four times. For Method 200.8, the tuning solution must be analyzed five times with a relative standard deviation less than 5%. Tuning criteria is listed in Table IV.

10.2.2. Check mass calibration and resolution daily.

10.2.2.1. Mass Calibration Check. The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

10.2.2.2. Mass Resolution Check. The resolution must be verified to be less than, or equal to, 0.9 amu full width at 10% peak height.

- 10.3. Initial Calibration: Calibrate the instrument for the analytes of interest according to manufacturer's instructions. Routine calibration and calibration verification levels are shown in Table V. The calibration should include a minimum of a blank and one standard. For a linear multi-point calibration curve, the correlation coefficient must be ≥ 0.995 for Method 200.8 and Method 6020. The correlation coefficient must be ≥ 0.998 for Method 6020A. Report the average of at least three integrations for both calibration and sample analysis. A calibration must be performed daily and each time the instrument is set up. Instrument run may be continued over periods exceeding 24 hours as long as calibration verification, interference check, and internal standard QC criteria are met. Calibration standard concentrations and/or vendors are subject to change.
- 10.4 Initial and Continuing Calibration Verification: ICV/CCV. Calibration accuracy is verified at the beginning of each analytical run by analyzing a second-source initial calibration verification (ICV) standard. A continuing calibration verification (CCV) standard is analyzed at a 10% frequency throughout the run. The ICV must be within 10% of the expected value, or the analysis is terminated. The CCV must be within 10% of the expected value for Method 6020 or 15% of the expected value for Method 200.8. Sample results may only be reported when bracketed by valid CCVs.

Note: The only exception is if the CCV recoveries are biased high and the associated sample is ND for the parameter(s) of interest. **This must be addressed in the project narrative.**

- 10.5 The CRI/LLCCV Method 6020A must be within the 70 – 130% recovery range and analyzed at the beginning and end of the analytical sequence. Please note the LLCCV (undigested) is still analyzed after the CRI. If any analyte is outside the range indicated, the sample may be re-analyzed once. If the results fall within the required values upon re-analysis, no further corrective action needs to be taken. If still outside the acceptable range, the analysis shall be terminated, the problem corrected, and the samples re-analyzed.
- 10.6 RL Verification Standard (CRI) Method 6020. An independent standard is analyzed after the ICB to monitor the lab's ability to produce reliable results at RL-level concentrations.

There is no set acceptance criteria established for this standard, but generally results should be within 50% of the expected value. Individual program requirements may vary.

- 10.7 ICB/CCB. The ICB/CCB solution is prepared with reagent water (ASTM Type I or equivalent) using the same acid matrix as the calibration standards. The Initial Calibration Blank (ICB) must be analyzed immediately following the ICV. The Continuing Calibration Blank (CCB) must be analyzed at a minimum frequency of 10% throughout the remainder of the analytical run. The ICB/CCB must fall within +/- the reporting limit from zero.

Note: The only exception is if the CCB recoveries are biased high and the associated sample is ND for the parameter(s) of interest. **This must be addressed in the project narrative.**

- 10.8 Interference Check Solutions (ICSA/ICSAB), Methods 6020 and 6020A only. The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Table II. The interference check solutions must be analyzed at the beginning of every analytical run and every 12 hours thereafter. The results of solution "A" and solution "AB" must be monitored for possible interferences.

- 10.8.1 Control limits of spiked analytes in the ICSA/ICSAB solution are $\pm 50\%$ of true value. Some projects may require control limits of $\pm 20\%$ of true value. Control limits of non-spiked analytes are \pm two times the reporting limit or less than 1 ug/L.

Note: It may not be possible to obtain absolutely clean ICSA/ICSAB standards. If contamination can be confirmed by another method (ICP/GFAA), acceptance criteria will be applied at that level and the data accepted.

- 10.9 Internal Standards. The intensities of all internal standards must be monitored throughout the run. The internal standard in the samples must be between 30% and 120% of the intensity of the calibration blank for Method 6020, 70-130% for Method 6020A, and between 60% and 125% for Method 200.8. If the sample falls outside of this criteria, perform the following procedures. First, evaluate nearby CCVs and CCBs. If sample internal standard recoveries appear to be related to instrument drift, then rerun affected samples. If sample internal standard recoveries appear to be primarily sample or matrix related, the run will be evaluated to determine if a dilution is needed. If dilutions are needed, then perform appropriate dilutions until the internal standard recoveries are within the method criteria. In no case may sample results be reported with internal standard recoveries greater than 40% higher than recoveries in surrounding CCVs/CCBs. Alternately, the run may be reprocessed with an alternative internal standard that is not in the samples and at an appropriate mass for the masses being reported. See Table I for a

list of Internal Standard analytes. See Table VII for the Internal Standard assignments.

- 10.10 Serial Dilution, **Methods 6020 and 6020A only.** One serial five-fold dilution must be analyzed per batch for each matrix. If the analyte concentration is within linear range of the instrument and sufficiently high (generally, a factor of 100 times above the reporting limit), the serial dilution must agree within 10% of the original analysis. If not, an interference effect must be suspected, the result is flagged, and included in the final report narrative. Samples identified as blanks cannot be used for serial dilution.
- 10.11 Post-Digestion Spike Addition (PDS), **Method 6020 (performed when required by client or project).** If the serial dilution fails to meet the acceptance criteria, a re-analysis of the serial dilution can be performed on a diluted sample provided that the concentration of the original sample after the dilution is above the requested reporting limit. If the serial dilution is still outside acceptance limits then a post digestion spike must be performed, as follows. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered within 75 - 125% of the known value. If the PDS fails to meet this criterion, matrix interference is suspected.

11. PROCEDURE

- 11.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo and is approved by a Technical Specialist. The Nonconformance Memo must be filed in the project file.
- 11.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP projects.
- 11.3 Sample Preparation
- 11.3.1 Preliminary acid digestion is required for groundwater, aqueous samples, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are requested. See SOPs NC-IP-010 and NC-IP-011 for preparation details.
- 11.3.2 For DoD work, refer to SOP NC-QA-016 for specific details.
- 11.4 Sample Analysis
- 11.4.1 Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.
- 11.4.2 Masses which would affect the data quality must be monitored during the

analytical run to determine the potential effects of matrix on a given element.

11.4.3 Dilute and re-analyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. The sample should be diluted to the approximate midrange of the linear range unless the dilution is for internal standard recoveries.

11.4.4 The analytical run sequence must be performed as follows to meet all quality control criteria:

- Warm-up
- Verify instrument performance
- Calibration blank
- Calibration standards
- ICV
- ICB
- RL verification standard
- LLCCV- 6020A
- ICSA (6020 and 6020A only)
- ICSAB (6020 and 6020A only)
- CCV
- CCB
- 10 Samples
- CCV
- LLCCV
- CCB

11.5 Analytical Documentation

11.5.1 Record all analytical information in LIMS, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2 All standards are logged into the LIMS standards and reagent module. All standards are assigned a unique number for identification.

11.5.3 Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4 Sample results and associated QC are uploaded into the LIMs. Level I and Level II technical reviews are done in LIMS.

12 DATA ANALYSIS AND CALCULATIONS

Note: The mean of three exposures is used to derive the sample concentrations used in the calculations in this section.

12.1 ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \times \left(\frac{\text{Found (ICV)}}{\text{True (ICV)}} \right)$$

12.2 CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \times \left(\frac{\text{Found (CCV)}}{\text{True (CCV)}} \right)$$

12.3 Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = 100 \times \left(\frac{\text{SSR} - \text{SR}}{\text{SA}} \right)$$

Where:

SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

Note: When sample concentration is less than the method detection limit, use SR = 0 for purposes of calculating % Recovery.

12.4 The relative percent difference (RPD) of sample duplicates are calculated according to the following equation:

$$\text{RPD} = 100 \times \left[\frac{(\text{DU1} - \text{DU2})}{(\text{DU1} + \text{DU2}) / 2} \right]$$

Where:

DU1 = Sample result

DU2 = Sample duplicate result

12.5 The final concentration for an aqueous sample is calculated as follows:

$$\text{Result (ug/L)} = \frac{(\text{C} \times \text{V1} \times \text{D})}{\text{V2}}$$

Where:

C = Concentration from instrument readout, ppb (mean of three exposures)

D = Instrument dilution factor

V1 = Final volume in liters after sample preparation

V2 = Initial volume of sample digested in liters

- 12.6 The concentration determined in digested solid samples when reported on a wet weight basis is as follows:

$$\text{Result (mg/kg)} = \frac{(C \times V \times D)}{W}$$

Where:

C = Concentration from instrument readout, ppb (mean of three exposures)

D = Instrument dilution factor

V = Final volume in liters after sample preparation

W = Weight, in g, of wet sample digested

- 12.7 Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13 METHOD PERFORMANCE

- 13.1 Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.
- 13.2 Refer to Table VI for the list of analytes that may be analyzed using this SOP for Methods 6020, 6020A, and 200.8. Additional analytes may be analyzed if all method-required QC is acceptable.
- 13.3 Training Qualifications
- 13.3.1 The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14 POLLUTION PREVENTION

- 14.1 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”.

15 WASTE MANAGEMENT

- 15.1 All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for “Waste Management and Pollution Prevention.”
- 15.2 Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.
- 15.3 Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.
- 15.4 Waste Streams Produced by the Method
 - 15.4.1 Acid waste consisting of sample and rinse solution generated by this method.
 - 15.4.1.1 Any sample waste generated must be collected and disposed of in the acid waste drum located in the Metals Lab.

16 REFERENCES

- 16.1 References
 - 16.1.1 Test Methods For Evaluating Solid Waste, EPA SW-846, 3rd Edition, Final Update II, Method 6020: “Inductively Coupled Argon Plasma - Mass Spectrometry”, Revision 0, September 1994
 - 16.1.2 Test Methods For Evaluating Solid Waste, EPA SW-846, Method 6020A: “Inductively Coupled Argon Plasma - Mass Spectrometry”, Revision 1, February 2007
 - 16.1.3 Environmental Monitoring Systems Laboratory, EPA Method 200.8, “Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry”, Revision 5.4, EMMC version
 - 16.1.4 [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version

16.1.5 TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version

16.1.6 [Corporate Quality Management Plan \(CQMP\)](#), current version

16.1.7 Revision History

Historical File:	Revision 0: 08/01/95	Revision 4.5: 07/30/08
	Revision 1: 06/06/01	Revision 4.6: 02/15/11
	Revision 3: 03/26/02	
	Revision 4: 03/06/03	
	Revision 4.1: 10/01/03	
	Revision 4.2: 01/08/04	
	Revision 4.3: 07/28/07	
	Revision 4.4: 07/30/08	

16.2 Associated SOPs and Policies, current version

16.2.1 QA Policy, [QA-003](#)

16.2.2 Acid Digestion of Soils, SW846 Method 3050B, [NC-IP-010](#)

16.2.3 Acid Digestion of Aqueous Samples by SW846 and MCAWW 200 Series Methods, [NC-IP-011](#)

16.2.4 Glassware Washing, [NC-QA-014](#)

16.2.5 Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)

16.2.6 Method Detection Limits and Instrument Detection Limits, [NC-QA-021](#) and [CA-Q-S-006](#)

16.2.7 Supplemental Practices for DoD Project Work, [NC-QA-016](#)

16.2.8 Standards and Reagents, [NC-QA-017](#)

16.2.6. Selection of Calibration Points, [CA-T-P-002](#)

16.2.7. Calibration Curves (General), [CA-Q-S-005](#)

17 MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1 Reporting limits

17.1.1 Refer to Table VI for associated reporting limits.

17.1.2 If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2 Method Deviations

17.2.1 Deviations from Method 6020

17.2.1.1 Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.1.2 The results of the calibration blank as well as all other blanks must be less than the reporting limit--not three times the instrument IDL.

17.2.1.3 Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks.

17.2.1.4 Internal standard recoveries may be less than 80% in CCVs and CCBs as long as QC criteria are met. Sample internal standard recoveries may never be greater than 40% higher than recoveries in associated CCVs/CCBs.

17.2.1.5 The method requires 1% nitric acid for the calibration blank, initial calibration standards, CCVs, ICV, and CRI. The laboratory uses 2% nitric acid and 5% hydrochloric acid.

17.2.1.6 The method states that the ICV should be prepared near the midpoint of the linear range. The laboratory prepares the standard near the midpoint of the calibration curve.

17.2.1.7 The method states in Section 8.5 that the dilution test sample result must be at least 100 times the concentration in the reagent blank. The laboratory uses 100 times the reporting limit as the criteria.

17.2.1.8 The ICSA/ICSAB solution is prepared every three months.

17.2.2 Deviations from Method 200.8

17.2.2.1 Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept in the laboratory.

17.2.2.2 The results of the calibration blank as well as all other blanks must be less than the reporting limit--not three times the instrument IDL.

17.2.2.3 Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by the analysis of blanks.

17.2.2.4 Resolution criteria of the mass calibration is met if the resolution criteria for Method 6020 is satisfied.

17.2.2.5 The concentration of most analytes in the LCS is 1000 µg/L. This is made from a commercially available stock solution and has all analytes at the same level. Verification records for this solution are kept in the laboratory.

17.2.2.6 Results are reported up to the verified linear range--not up to only 90% of the linear range.

17.2.2.7 The method requires 1% nitric acid for the calibration blank, initial calibration standards, CCVs, ICV, and CRI. The laboratory uses 2% nitric acid and 5% hydrochloric acid.

17.2.2.8 The tuning solution and internal standard solution are prepared with 2% nitric acid. The method states 1% nitric acid.

17.2.2.9 The method requires a dilution prior to analysis to adjust the chloride concentration in the sample. Due to newer instrument technology, this dilution is no longer needed.

17.3 Tables

TABLE I: Recommended Internal Standards

Li
Sc
Y
Rh
In
Tb
Ho
Bi
Ge

TABLE II: Interference Check Sample Components and Recommended Concentrations

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	50	50
Ca	50	50
Fe	50	50
Mg	50	50
Na	50	50
P	50	50
K	50	50
S	50	50
C	100	100
Cl	500	500
Mo	1.0	1.1
Ti	1.0	1.1
As	0.0	0.1
Cd	0.0	0.1
Cr	0.0	0.1
Co	0.0	0.1
Cu	0.0	0.1
Mn	0.0	0.1
Ni	0.0	0.1
Se	0.0	0.1
Ag	0.0	0.1
V	0.0	0.1
Zn	0.0	0.1

TABLE III: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are two groups of suggested solutions which cover a typical mass calibration range.

Element	Concentration (µg/L)
Mg	10
Rh	10
Pb	10
Li	10
Co	10
In	10
Tl	10

Element	Concentration (µg/L)
Be	10
Mg	10
Co	10
In	10
Pb	10
Ba	10
Ce	10

TABLE IV: Suggested Tuning and Response Factor Criteria Minimum Response from Tuning Solution

**Minimum Response from Tuning Solution
With a Peristaltic Pump Speed of 25 RPM**

Be	> 8,000
In	>300,000
Pb	> 100,000
Co	> 100,000

Mg > 10,000

Suggested Mass Calibration

Be	9.0122
Mg	23.98
Rh	102.91
Pb	207.98
Li	7.016
Co	58.9332
In	114.904
Tl	204.9744

TABLE V: ICP/MS Calibration and Calibration Verification Checklist
Suggested Levels in µg/L

Element	Calibration		ICV	CCV
	1	2		
Aluminum	500	1000	400	500
Antimony	100	200	80	100
Arsenic	100	200	80	100
Barium	100	200	80	100
Beryllium	100	200	80	100
Boron	100	200	80	100
Cadmium	100	200	80	100
Calcium	50000	100000	40000	50000
Chromium	100	200	80	100
Cobalt	100	200	80	100
Copper	100	200	80	100
Iron	25000	50000	20000	25000
Lead	100	200	80	100
Manganese	500	1000	400	500
Magnesium	50000	100000	40000	50000
Molybdenum	100	200	80	100
Nickel	100	200	80	100
Potassium	50000	100000	40000	50000
Selenium	100	200	80	100
Sodium	50000	100000	40000	50000
Silver	100	200	80	100
Strontium	100	200	80	100
Thallium	100	200	80	100
Tin	100	200	80	100
Titanium	100	200	80	100
Tungsten	100	200	80	100
Vanadium	100	200	80	100
Zinc	100	200	80	100

This procedure has been developed for additional elements. Additional elements may be included in the calibration solution at the appropriate levels. Levels may be adjusted to meet specific regulatory or client programs.

TABLE VI: Suggested ICP/MS Reporting Limits
Water 6020, 6020A, and 200.8
Solid 6020 and 6020A (only)

Compound	RL	Units	RL	Units
Aluminum	50	ug/L	5000	ug/kg
Antimony	2	ug/L	200	ug/kg
Arsenic	5	ug/L	500	ug/kg
Barium	1	ug/L	100	ug/kg
Beryllium	1	ug/L	100	ug/kg
Boron	20	ug/L	2000	ug/kg
Cadmium	1	ug/L	100	ug/kg
Calcium	1000	ug/L	100000	ug/kg
Chromium	2	ug/L	200	ug/kg
Cobalt	1	ug/L	100	ug/kg
Copper	2	ug/L	200	ug/kg
Iron	50	ug/L	5000	ug/kg
Lead	1	ug/L	100	ug/kg
Magnesium	1000	ug/L	100000	ug/kg
Manganese	1	ug/L	100	ug/kg
Molybdenum	2	ug/L	200	ug/kg
Nickel	2	ug/L	100	ug/kg
Potassium	1000	ug/L	100000	ug/kg
Selenium	5	ug/L	500	ug/kg
Silver	1	ug/L	100	ug/kg
Sodium	1000	ug/L	100000	ug/kg
Strontium	10	ug/L	1000	ug/kg
Thallium	1	ug/L	100	ug/kg
Tin	10	ug/L	1000	ug/kg
Titanium	10	ug/L	1000	ug/kg
Tungsten	10	ug/L	1000	ug/kg
Vanadium	20	ug/L	500	ug/kg
Zinc	20	ug/L	2000	ug/kg

TABLE VII: Internal Standard Assignments

Standard Mode Internal Standards: 6Li and 45Sc		
CCT Mode Internal Standards: 45Sc, 72Ge, 115In, 159Tb*, 165Ho, 209Bi*		
*Not used on a daily basis but may be used as an alternative or additional internal standard		
Mass_Element	Associated Internal Standards	Possible Alternatives
6Li		
9Be	6Li	45Sc Standard
10B	6Li	45Sc Standard
23Na	45Sc CCT	
25Mg	45Sc CCT	
27Al	45Sc CCT	
39K	45Sc Standard	6Li
43Ca	45Sc Standard	6Li
45Sc Standard		
45Sc CCT		
47Ti	45Sc CCT and 72Ge	Ge Only
51V	45Sc CCT and 72Ge	Ge Only
52Cr	45Sc CCT and 72Ge	Ge Only
55Mn	45Sc Standard	6Li
56Fe	45Sc CCT and 72Ge	Ge Only
59Co	45Sc CCT and 72Ge	Ge Only
60Ni	45Sc CCT and 72Ge	Ge Only
65Cu	45Sc CCT and 72Ge	Ge Only
66Zn	45Sc CCT and 72Ge	Ge Only

72Ge		
75As	72Ge and 115In	Ge Only or 115In Only
78Se	72Ge and 115In	Ge Only or 115In Only
88Sr	72Ge and 115In	Ge Only or 115In Only
95Mo	72Ge and 115In	Ge Only or 115In Only
107Ag	72Ge and 115In	Ge Only or 115In Only
111Cd	72Ge and 115In	Ge Only or 115In Only
115In		
118Sn	115In and 165Ho	115In Only, 209 Bi Only, 159Tb Only, or using any combination of 115In, 159Tb, 165Ho, and/or 209Bi
121Sb	115In and 165Ho	115In Only, 209 Bi Only, 159Tb Only, or using any combination of 115In, 159Tb, 165Ho, and/or 209Bi
137Ba	115In and 165Ho	115In Only, 209 Bi Only, 159Tb Only, or using any combination of 115In, 159Tb, 165Ho, and/or 209Bi
182W	115In and 165Ho	115In Only, 209 Bi Only, 159Tb Only, or using any combination of 115In, 159Tb, 165Ho, and/or 209Bi
205Tl	115In and 165Ho	115In Only, 209 Bi Only, 159Tb Only, or using any combination of 115In, 159Tb, 165Ho, and/or 209Bi
208Pb	115In and 165Ho	115In Only, 209 Bi Only, 159Tb Only, or using any combination of 115In, 159Tb, 165Ho, and/or 209Bi
209Bi		
<i>The analyst has the option to associate an alternative Internal Standard with an element if acceptance criteria is not met.</i>		
<i>Generally, the mass of the internal standard should be no more than 50 amu of the mass of the measured analyte, however,</i>		
<i>Please refer to the above-listed alternatives for possible examples.</i>		

APPENDIX A

OPERATION INSTRUCTION – ICPMS INSTRUCTIONS

Procedure

1. Instrument Set-up

- 1.1 Configure the X Series with the standard sample introduction equipment, i.e., a glass concentric nebulizer, glass impact bead spray chamber, and a one-piece torch with 1.5mm ID injector tube. A Peltier spray chamber-cooling unit is optional. Ensure the Xi interface cones are fitted. They can be identified as follows:
- Xi Sampler - 1.1 mm orifice, no nipple, no holes around the flat circumference
 - Xi Skimmer - Small pointed skimmer mounted in a copper adapter with two screws

- 1.3 Switch the instrument into the *Operate* state by clicking the *ON* button at the top of the screen. During the automated ignition sequence, the following processes occur:

- Torch purge with argon gas
- RF power match
- Plasma ignition
- Slide valve open
- Electronics on

This process takes about two minutes. Upon successful ignition, the software will display *Operate* in the *Instrument State* bar. In the event of unsuccessful ignition, the software will display an error message and/or place a message in the *Technician Event Log*. Upon unsuccessful ignition, inspect the sample introduction equipment and torch, ensuring a good gas-seal at each connection and ensuring the torch is not misaligned or damaged. If all appears satisfactory, the ignition may be attempted again. If the ignition process consistently fails, contact your local service agent for advice.

- 1.4 Once the instrument is in the *Operate* state, it must be left for 30 minutes to reach thermal equilibrium prior to starting analytical measurements. The optimization (tuning), performance testing, and instrument set-up calibrations may be performed after 15 minutes. Ensure the peristaltic pump is operated at a default analytical speed of 40%. This is done by clicking on *Instrument, Configurations, Configuration Editor, View*

Selected Accessories (network icon), *Peristaltic Pump*, *Connect* (chain icon). Set pump speed to 40% using the slider bar. Click *OK* to close the dialogue box.

- 1.5 During the initial 15 minutes, the system can be “conditioned” by aspirating the system thoroughly with 5% HCL and 2% nitric acid solution prior to continuing.
- 1.6 Instrument tuning (optimization) is performed using a 20 µg/L Tune Solution aspirated through the sample uptake tube. Optimization may not be necessary from day to day if the sample introduction system and cones have not been adjusted in any way, and if the instrument fulfills the performance requirements given below. Tune the instrument manually or use *Autotune* while aspirating a 20 µg/L Tune Solution with the sample uptake probe in the tune solution and the internal standard probe in a 5%HCL and 2%HNO₃ solution. *Autotune*, using an appropriately defined sequence, is advised. If the CCT gas mode is being used, along with the standard mode for particular elements, both the CCT gas and the standard mode will need to be tuned. See Tables III and IV for additional tuning information.

If the above criteria are not met, do not proceed. Check that the tune solution was prepared as per instructions, and remake, if necessary. If the sensitivity is below the minimum requirement, a new detector plateau may be required, the cones may require cleaning, or the nebulizer or sample uptake lines may have become blocked, or may not be properly clamped on the peristaltic pump. If the CeO/Ce ratio is 0.03, the nebulizer gas flow can be reduced and/or the sampling depth increased, obtaining a corresponding reduction in oxide formation. Recheck the above parameters after taking any remedial action.

- 1.7 Save the satisfactory instrument settings by clicking on the disk icon on the Tune page. Note this is not necessary if *Autotune* has been used, as the instrument settings are saved automatically (unless manual adjustments have been made after autotuning).
- 1.8 Perform a cross-calibration (and mass-calibration and detector voltage setup, if required). Note: Retuning may be necessary after performing this routine.
- 1.9 Aspirate Tune solution and run a *Performance Report* to confirm the mass-calibration, resolution, minimum sensitivity, and maximum cerium oxide requirement, and to verify instrument stability. The performance report acquires five consecutive one-minute runs and calculates the percentage relative standard deviation (RSD) of the five measurements for each isotope. The RSD of the elemental analytes in the performance report must be < 5%. If the performance report fails, check:
 - Liquid uptake tubes for kinks or other damage
 - Condition and position of the peristaltic pump tubing
 - Tightness of the peristaltic pump clamp screws (these must be just tight enough to draw liquid through the tube smoothly)

- Joints of all sample introduction components, ensuring a good seal
- Nebulizer for blockage
- Salt deposition on cones

Remedy the above as necessary, and repeat the test. Note: Retuning may be required if any sample introduction components are adjusted or replaced.

If the measured mass position for each mass in the performance report is not within ± 0.1 amu of the nominal mass position, a new mass calibration must be performed.

2. Sample Analysis

- 2.1 Open the method template by clicking on *Templates* and then <Test America North Canton Multimode>. The method template will be opened. This contains all the saved analytical parameters, and only the sample list need be amended.
- 2.2 Go to *Sample List*. This grid contains all the information about calibration, QC, and samples to be analyzed. The calibration and QC concentration information are already stored. Enter all unknown samples into the list in the appropriate order below the existing calibration and QC samples by overwriting the sample label fields. Delete any QC samples that do not apply to the required method. (If sample list changes are to be made permanent to the method, save the method as a *Template* by going to *File, Save As Template*. Enter a new name to create an amended method, or use the same name to overwrite the current one.)
- 2.3 Once all the sample information is added, check that the required autosampler positions have been correctly entered. Amend as necessary. To sequentially renumber positions, add the correct position required for the initiation of the sequence and right mouse click on the first correctly numbered cell. A pop-up menu will appear. Select *Renumber autosampler positions* from this. Ensure all samples have one survey run and three main runs.
- 2.4 Save the experiment run by clicking on the *File* menu, then *Save As*. Enter the required file name, e.g., 100107, and click *Save*.
- 2.5 To print the sample list, go to *Reports*, and check the *Sample List* box. Click the refresh icon. The sample list will be displayed in a printable format. Press the print icon.

3. Loading the Autosampler

- 3.1 Pour the required samples into pre-cleaned 15 mL polypropylene test tubes. To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination.

- 3.2 Pour blanks, standards, and QCs (positioned in rack 0) into pre-cleaned 50 mL polypropylene tubes. To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination. Note that 5 % HCL and 2% nitric acid is used as the calibration blank, ICB, and CCB.
- 3.3 Place the tubes for each sample into the appropriate position in the rack according to the sample list. Note that the autosampler works on a two-dimensional grid position system by rack number (0-4).

4. Initiating Analysis

- 4.1 Place the sample probe into the autosampler arm and the internal standard probe into the internal standard solution.
- 4.2 Go to *Instrument, Tune*, and click on the accessories dialog icon. Click on *Autosampler*, and then on the chain icon to connect. The autosampler should initialize. Ensure the probe is at the correct height by positioning it so its tip just protrudes through the hole in the bottom of the arm. Click on the *Go to Wash* icon (faucet) to send the probe to the wash station. Ensure the wash solution is being correctly delivered to the wash station via the peristaltic pump at the rear of the autosampler. Allow at least two minutes for the liquid to be delivered to the sample introduction system.
- 4.3 Click on the experiment to be run. Click the *Queue* icon, then *Append*, and *OK*. The analysis has now been initiated.
- 4.4 To monitor the progress of the analysis, right-mouse click on the *MS* icon at the bottom-right of the screen and select *Open Service Window* from the pop-up menu. The Service Window hovers over the current application window until moved or closed and displays the current instrument activity. This window is also used **to stop an analysis**, if required. This is done by clicking on the ***XQ* icon**.
- 4.5 To view results as they are generated, click on the experiment icon and go to the *Results* tab. Click on the *Refresh* button or the refresh icon (green circular arrows on a page) to calculate the results from the data obtained.
- 4.6 To view calibration plots, click on the *Calibration Data* tab. The calibration for each analyte can be viewed by clicking on the required isotope in the *Analyte* box. Each subsequent set of calibrations (calibration block) can be displayed by selecting the required calibration block from the drop-down combo box, e.g., *FQ Block 1*, *FQ Block 2*, etc. FQ denotes a Fully-Quantitative calibration, and SQ denotes a Semi-Quantitative calibration, i.e., a response curve generated from the *FQ* calibrations. The SQ response curve is used to calculate semi-quantitative concentrations if required.

- 4.7 To view data, click on the *Numerical Results* tab. The *Analyte Dilution Conc.* tab is a tabular display of the calculated corrected concentrations for each analyte. These values have been corrected for internal standardization, external drift correction (if used), and dilution (where entered). The *Mass Uncorrected ICPS* tab shows the uncorrected raw data for each measured mass in units of integrated counts per second (ICPS). The *Analyte ICPS* tab shows integrated counts per second data that has been mathematically corrected for blank deduction, internal standardization, drift correction (if used), and dilution (as appropriate). The *Survey* tabs show the data integrated from the survey scan for each sample. Any concentrations displayed in the survey page will be semi-quantitative only.
- 4.8 To edit the amount of data on screen (filter the results display), click on the filter icon (funnel and lightning). Alter the numerical values or the check boxes to select the required data to display, and click on *OK*. To jump directly to a particular sample of interest, find the sample in the drop-down combo box at the top of the data display, and click on it.
- 4.9 To display mass-spectra, click on the *Spectra* tab. Display the spectrum for a particular sample by double-clicking on the sample name in the selection box on the left of the screen. Note several spectra may be overlaid by double-clicking on each sample to be displayed. To zoom into a particular area, click the zoom icon (magnifying glass), and click and drag on the spectral display to zoom into the required area. The dashed-lines represent data acquired in the analogue mode of the detector whilst the solid-lines represent pulse-count data. To remove the noise associated with analogue detection at low signal levels, point at the display and right-mouse click to bring up a menu. Go to *View Options*, and then click on *Eliminate Analogue Noise*. To identify a peak, click on it and wait for the options for that mass to be displayed in the box above the spectral display. To fingerprint a spectrum, double-click on the species to fingerprint in the options box. This will overlay the isotopic pattern for the selected species, based on the lowest relative intensity signal for the pattern masses. The spectra may be navigated by using the arrow buttons above the display. Allow the arrow cursor to hover over each button for an on-screen explanation of its function.

5. Post-Analysis Data Processing

5.1 Internal Standards

- Check the internal standard recovery percentage for each internal standard isotope used for every sample. The percentage for each isotope must be within the range 30 - 120% for Method 6020 and 60 – 125% for Method 200.8.
- If above 120%, check that the other internal standard isotopes show similar deviation. If not, this may be due to the presence of the internal standard element in the sample. This is particularly common with the isotopes of Li, Sc, and Y in

environmental materials. If this is the case, the affected internal standard isotope may be excluded for the sample affected as follows. Go to the *Sample List*.

- Find the sample affected, and select it in the list by clicking on the box in the left-hand column. Click *Show Advanced*, and go to *Internal Standards*. Click on *New Internal Standard Set*. Select the affected isotope(s) in the *Internal Standards* box on the right. Remove the affected isotope from the *Internal Standards* box by using the left-hand arrow button (<<). Recalculate the results for this sample by going back to *Results*, and clicking on *Refresh*.
- If any internal standard isotope is outside the range 30-120% and all other internal standard isotopes show similar values for that sample, the instrument may have drifted; or the sample may be producing a suppression or enhancement effect. Find the nearest blank following the sample in question and check its internal standard results. If these are similarly reduced or elevated, the instrument has drifted, and the samples must be re-analyzed from the last compliant blank. If the blank does not exhibit similar drift, the sample must be producing a suppression or enhancement effect due to its matrix. In this case, the sample must be re-analyzed after a five-fold (1:5) or a ten-fold (1:10) dilution to reduce the matrix effect.

6. General protocols

- 6.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. The Nonconformance Memo must be filed in the project file.
- 6.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.
- 6.3 An analytical run will consist of all customer samples and quality control samples analyzed under a daily initial calibration. Each new initial calibration will begin a new analytical run.
- 6.4 Type in the QC and sample information into the autosampler table.

7. Initial Calibration

- 7.1 Open a new dataset using the date of analysis as the file name.

- 7.2 Open the appropriate method if one already exists, or create a new one for the analytes to be quantitated in the run. Solicit the assistance of a senior ICP-MS operator in creating a new method.
- 7.3 All masses which could affect data quality should be monitored to determine potential interferences, either simultaneously during an analytical run, or in a separate scan.
- 7.4 Internal standards are added to all standards and samples by the instrument prior to analysis.
- 7.5 Use of an existing autosampler table is suggested.
- 7.6 Calibration consists of a blank and two calibration standards in accordance with the manufacturer's procedure. Use the average of three integrations for both calibration and sample analyses.

8. The order of analysis for the initial QC samples and calibration should be:

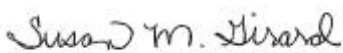
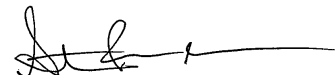
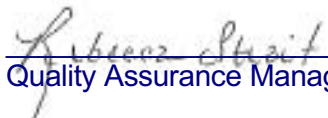

STD1 (Calibration Blank)
STD2 (Calibration Standard)
STD3 (Calibration Standard)
STD4 (Calibration Standard)
ICV
ICB
CRI (Reporting Limit Verification Standard)
ICSA (Interference check solution)
ICSAB (Interference check solution)
CCV
CCB
Prep QC such as LCS or MB, followed by samples (up to 10)
Rinse
CCV
CCB

To continue the analytical run, add an additional ten runs followed by a rinse and CCV/CCB.

**Title: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS
AND SOLID SAMPLES BY COLD VAPOR ATOMIC
ABSORPTION SPECTROSCOPY**

[Method: MCAWW Method 245.1, SW846 Method 7470A,
SW846 7471A, and 7471B]

Approvals (Signature/Date):

 _____ Technology Specialist	03/19/13 _____ Date	 _____ Health & Safety Coordinator	03/19/13 _____ Date
 _____ Quality Assurance Manager	03/19/13 _____ Date	 _____ Laboratory Director	03/19/13 _____ Date

This SOP was previously identified as SOP No. NC-MT-014, Rev 1-A, dated 04/17/12

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1. SCOPE AND APPLICATION

- 1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW846 Method 7470A, MCAWW Method 245.1 Method 7471B, and Method 7471A.
- 1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants and potassium permanganate has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity, and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation, and volume of sample used.
- 1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, TCLP, and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed; however, Method 7471A is usually the method of choice. All matrices require sample preparation prior to analysis.
- 1.4. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters, and domestic and industrial wastes. All matrices require sample preparation prior to analysis.
- 1.5. Methods 7471A and 7471B are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits, wastes, wipes, biological material, and sludge-type materials. All matrices require sample preparation prior to analysis.
- 1.6. The TestAmerica North Canton reporting limit for mercury in aqueous matrices is 0.0002 mg/L except for TCLP or SPLP leachates for which the reporting limit is 0.002 mg/L. The TestAmerica North Canton reporting limit for mercury in solid matrices is 0.1 mg/kg.
- 1.7. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

- 2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric (aqueous samples), or hydrochloric and nitric acids (soil samples). Organic mercury compounds are oxidized with potassium permanganate (aqueous and soil samples) and potassium persulfate (aqueous samples), and the mercury reduced to its elemental state with stannous chloride 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 is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

- 4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control (QC) section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Chemical and physical interferences may be encountered when analyzing samples using this method.
- 4.3. Potassium permanganate, which is used to break down organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.
- 4.4. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.
- 4.5. Chlorides can cause a positive interference. Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (maximum 25 mL); because during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride

- 4.6. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the

mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

- 4.7. Samples containing high concentrations of oxidizable organic materials, as evidenced by high Chemical Oxygen Demand (COD) levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.
- 4.8. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. Refer to Appendix B for Contamination Control Guidelines.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.
- 5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- 5.3. 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 Material Safety Data Sheet (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
Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 g/m ³ 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	1 mg/m ³ - TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may

	Dehydrator Poison		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.
Hydroxyl-amine Hydro-chloride	Corrosive Poison	None	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. Corrosive to the eyes. Irritant and possible sensitizer. May cause burns to the skin.
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.
Potassium Permanganate	Oxidizer	5 mg/m ³ 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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant

gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.

- 5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.
- 5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.
- 5.7. Do not look directly into the beam of the Hg lamp. The Ultra Violet (UV) light that these lamps radiate is harmful to the eyes.
- 5.8. Cylinders of compressed gas must be handled with caution in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory, and the gas led to the instrument through approved lines.
- 5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. **EQUIPMENT AND SUPPLIES**

- 6.1. Temperature-controlled water bath (capable of maintaining temperature of 90- 95 °C).
- 6.2. Atomic Absorption Spectrophotometer equipped with:
 - 6.2.1. Absorption cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.
 - 6.2.2. Mercury-specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL)
 - 6.2.3. Peristaltic pump which can deliver 1 L/min air
 - 6.2.4. Flowmeter capable of measuring an airflow of 1 L/min
 - 6.2.5. Recorder or printer

6.2.6. Drying device to prevent condensation in cell.

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique may be substituted for the atomic absorption spectrophotometer.

- 6.3. Plastic bottles – 250 mL
- 6.4. Nitrogen or argon gas supply, welding grade or equivalent
- 6.5. Calibrated automatic pipettes
- 6.6. Class A volumetric flasks
- 6.7. Top-loading balance, capable of reading up to two decimal places
- 6.8. Thermometer (capable of accurate readings at 95 °C)
- 6.9. Disposable cups or tubes

7. REAGENTS AND STANDARDS

- 7.1. Reagent water must be produced by a Millipore Deionized Water (DI) system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.
- 7.2. Stock (10 ppm) mercury standards are purchased as custom solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Additional information can be found in SOP NC-QA-017. Refer to the reagent module in the Laboratory Information Management System (LIMS) for details on standard preparation.
- 7.3. Working mercury standard (0.1 ppm): Take 1 mL of the stock mercury standard (Section 7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO₃. This acid (150 uL of concentrated HNO₃) must be added to the flask/bottle before the addition of the stock standard aliquot. Refer to the reagent module in LIMS for details on standard preparation.
- 7.4. The calibration standards must be prepared fresh daily from the working standard (Section 7.3) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury

standard into sample preparation bottles and proceeding as specified in Section 11.1. The laboratory control sample (LCS) solution is prepared by transferring 5.0 mL of working standard (Section 7.3) into sample preparation bottles and proceeding as specified in Section 11.1. Refer to the reagent module in LIMS for details on standard preparation.

Note: Alternate approaches to standard preparation may be taken, and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I (Appendix A) are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

- 7.5. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards.
- 7.6. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.
- 7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better
- 7.8. Hydrochloric acid (HCl), concentrated, trace metal grade or better
- 7.9. Sulfuric acid (H_2SO_4), concentrated, traces metal grade or better.
- 7.10. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3 .
- 7.11. Stannous chloride solution: Add $50\text{g} \pm 0.5\text{g}$ of stannous chloride and 25 mL of concentrated HCl , and bring to a final volume of 500 mL with DI water.

Note: Stannous sulfate may be used in place of stannous chloride. Prepare the stannous sulfate solution according to the recommendations provided by the instrument manufacturer.
- 7.12. Sodium chloride-hydroxylamine hydrochloride solution: Add $240\text{g} \pm 0.5\text{g}$ of sodium chloride and $240\text{g} \pm 0.5\text{g}$ of hydroxylamine hydrochloride to every 2000 mL of reagent water.
- 7.13. Potassium permanganate, 5% solution (w/v): Dissolve 100g of potassium permanganate for every 2000 mL of reagent water.
- 7.14. Potassium persulfate, 5% solution (w/v): Dissolve 100 g of potassium persulfate for every 2000 mL of reagent water.

8 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1 Sample holding time for mercury is 28 days from time of sample collection to the time of sample analysis.
- 8.2 Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.
- 8.3 Soil samples and biological material do not require preservation, but must be collected in wide-mouth glass jars with PTFE-lined lids and stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ (and/or freezing for tissues) until the time of analysis.

9 QUALITY CONTROL

- 9.1 Initial Demonstration of Capability
- 9.2 Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.
 - 9.2.1 Four aliquots of the laboratory check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.
- 9.3 Preparation Batch - A group of up to 20 samples, excluding QC Samples (Laboratory Control Sample (LCS), Method Blank (MB), Matrix Spike (MS), Matrix Spike Duplicate (MSD)), that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank (MB), a Laboratory Control Sample (LCS) and a matrix spike/matrix spike duplicate (MS/MSD). All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes. In some cases, at client request, it may be appropriate to process a matrix spike (MS) and sample duplicate in place of the matrix spike/matrix spike duplicate (MS/MSD). If clients specify specific samples for matrix spike/matrix spike duplicate (MS/MSD), the batch may contain multiple matrix spike/matrix spike duplicate (MS/MSD) pairs.
- 9.4 Method Blank (MB) - One method blank(MB) must be processed with each preparation batch. The method blank(MB) consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank (MB) is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte

concentrations or false positive data. The method blank (MB) must not contain any analyte of interest at, or above, the reporting or at, or above, 10% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of ten times higher than the method blank (MB) contamination level).

Note: For Ohio VAP projects, the result must be below the reporting limit or samples must be redigested and re-analyzed unless the samples are non-detect.

- Redigestion and re-analysis of all samples associated with an unacceptable method blank (MB) is required when reportable concentrations are determined in the samples (see exception noted above).
- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank (MB), the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**
- If the above criteria are not met and re-analysis is not possible due to limited sample quantity, then the sample data must be qualified. **This anomaly must be addressed in the project narrative.**

9.5 Laboratory Control Sample (LCS) – One laboratory control sample (LCS) must be processed with each preparation batch. The laboratory control sample (LCS) is used to monitor the accuracy of the analytical process. Ongoing monitoring of the laboratory control sample (LCS) results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The laboratory control sample (LCS) must be carried through the entire analytical procedure. If the laboratory control sample (LCS) is outside established control limits, the system is out of control and corrective action must occur. See Section 12 for the laboratory control sample (LCS) calculation.

- In the instance where the laboratory control sample (LCS) recovery is greater than the upper control limit and the sample results are less than RL, the data may be reported. Such action must be addressed in the project narrative. For Method 245.1, the laboratory control sample (LCS) must be 85% - 115%. For Method 7471B, the laboratory control sample recovery must be 80%- 120%.
- Corrective action must be redigestion and re-analysis of the batch unless the client agrees that other corrective action is acceptable. For Ohio VAP projects the corrective action must be redigestion and reanalysis of the batch.

9.6 Additional information on QC samples can be found in QA Policy QA-003. Ohio VAP projects must reference this SOP instead of policy QA-003 for information on QC samples.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One matrix spike/matrix spike duplicate (MS/MSD) pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the matrix spike (MS)) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of, or in addition to, matrix spike/matrix spike duplicates (MS/MSDs). The matrix spike/matrix spike duplicate (MS/MSD) results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for matrix spike/matrix spike duplicate (MS/MSD) analysis. Spiking levels are provided in Table I (Appendix I). See Section 12 for the matrix spike/matrix spike duplicate (MS/MSD) and Relative Percent Difference (RPD) calculation.

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the laboratory control sample (LCS). A control limit of $\pm 70 - 130\%$ for Method 245.1, and 20% RPD must be applied to the matrix spike/matrix spike duplicate (MS/MSD). A control limit of 80-120% for Method 7471B and 20% RPD must be applied to the MS/MSD. If the laboratory control sample (LCS) recovery is within control limits, then the laboratory operation is in control and the results may be accepted. Client specific matrix spike/matrix spike duplicate (MS/MSD) samples may require corrective action. Such action must be addressed in the project narrative by means of a non-conformance memo (NCM). If the recovery of the laboratory control sample (LCS) is outside of control limits, corrective action must be taken. Corrective action must include redigestion and re-analysis of the batch. Matrix spike/matrix spike duplicate (MS/MSD) results which fall outside the control limits must be addressed in the narrative.
- If the native analyte concentration in the matrix spike/matrix spike duplicate (MS/MSD) exceeds four times the spike level for that analyte, the recovery data are reported with a "4" as a flag. In the event a matrix spike/matrix spike duplicate (MS/MSD) analysis is not possible, notation in the project narrative is required.

9.8 Control Limits

9.8.1 Control limits are established by the laboratory as described in SOP NC-QA-018

9.8.2 Control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMS

9.9 Method Detection Limits (MDLs) and MDL Checks

9.9.1 MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.9.2 MDLs are easily accessible via LIMS

9.10 Nonconformance and Corrective Action

9.10.1 Any deviations from QC procedures must be documented as a nonconformance
Procedural deviations are not allowed for Ohio VAP Projects.

10 CALIBRATION AND STANDARDIZATION

10.1 Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2 Due to the differences in preparation protocols, separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3 Calibration must be performed daily and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4 Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the CVAA instrument manual for detailed setup and operation protocols.

10.5 Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a calibration blank. One standard must be at, or below, the reporting limit. Analyze standards in ascending order beginning with the calibration blank. Refer to Section 7 and Table I for additional information on preparing calibration standards and calibration levels.

10.6 The calibration curve must have a correlation coefficient of ≥ 0.995 , or the instrument must be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient. NOTE: If any digested calibration standard does not meet SW846 criteria, all associated Ohio VAP samples must be redigested.

10.7 Initial Calibration Verification/Initial Calibration Blank (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% of the true value for that solution. An ICB is analyzed immediately following the ICV to

monitor low level accuracy and system cleanliness. The ICB result must fall within \pm the reporting limit (RL) from zero. See Section 12 for the ICV calculation. If either the ICV or ICB fail to meet criteria, the analysis must be terminated, the problem corrected, and the instrument recalibrated (see Section 11.2.6 for required run sequence). The calibration curve standards are reanalyzed to determine if the failure was instrument related. If the cause of the ICV or ICB failure was not directly instrument-related, the corrective action must include re-digestion of the ICV, ICB, CRA, CCV, and CCB with the calibration curve. For Ohio VAP, the sample batch must be redigested.

- 10.8 Continuing Calibration Verification/Continuing Calibration Blank (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV.

10.8.1 For Method 245.1, the CCV must be 5% immediately following the calibration. All other CCVs for Method 245.1 must be 90-110%.

10.8.2 The CCV result for Methods 7470A, 7471A, and 7471B must fall within 20% of the true value for that solution. See Section 12 for the CCV calculation.

10.8.3 A CCB is analyzed immediately following each CCV (see Section 11.2.6 for required run sequence). The CCB result must fall within \pm RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. If the CCV/CCB is biased high and the sample results associated with the CCV/CCB are below the requested reporting limit, then the results can be reported. Sample results may be reported when bracketed by valid CCV/CCB pairs. If any digested calibration standard does not meet SW846 criteria, all associated Ohio VAP samples must be redigested.

- 10.9 Detection Limit Standard (CRA) - To verify linearity at the reporting limit, a CRA standard is run at the beginning of each sample analysis run after the ICV/ICB. The CRA standard mercury concentration is 0.2 ug/L. It is recommended that the recovery be \pm 50% of the true value, or the standard is either rerun or the problem corrected and the instrument recalibrated. The CRA is only required when requested.

- 10.10 For DoD work, refer to SOP NC-QA-016 for specific details.

11 PROCEDURE

- 11.1 Standard and Sample Preparation- Solids

11.1.1 All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples.

11.1.2 Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (Section 7.3) into a series of sample digestion bottles. The ICB/CCB consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. For the ICV, transfer a 2.5 ml aliquot of the working standard. The ICV working standard must be made from a source other than that used for the calibration standards. For the CCB, transfer a 5 mL aliquot of the working standard into a sample digestion bottle.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

11.1.3 Add reagent water to each standard bottle to make a total volume of 10 mL. Continue preparation as described under Section 11.2 below.

11.1.4 Transfer 0.6g of a well-mixed sample into a clean sample digestion bottle. Continue preparation as described under Section 11.2.

11.2 Water Bath Protocol – Solid Samples

11.2.1 To each laboratory control sample (LCS) **standard** bottle, add 5 mL of reagent water, 5 mL of aqua regia, and 5 mL of the working mercury standard (0.1 ppm) (see Section 7.3).

11.2.2 To each **sample** and Method Blank (MB) bottle, add 10 mL of reagent water and 5 mL of aqua regia.

11.2.3 Heat for two minutes in a water bath at 90 - 95 ° C. For Method 7471B, remove from water bath and allow to cool before the addition of distilled water and potassium permanganate solution.

11.2.3.1 Add 40 mL of distilled water.

11.2.3.2 Add 15 mL of potassium permanganate solution. Cover containers. For Method 7471B, let samples stand at least 15 minutes prior to heating.

11.2.3.3 Heat for 30 minutes in the water bath at 90 - 95 °C.

11.2.3.4 Cool

11.2.3.4 Add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.2.3.5 To each **standard, quality control sample**, and sample bottle, add 50 mL of reagent water.

11.2.3.6 Continue as described under Section 11.5.

11.3 Standard and Sample Preparation Waters

11.3.1 All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure as well as the field samples. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (Section 7.3) into a series of 100 ml Class A volumetrics, then dilute to volume. For the ICV, use a 2.5 ml aliquot of the working standard. The ICV working standard must be made from a source other than that used for the calibration standards. For the CCV, transfer a 5 mL aliquot of the working standard into a Class A volumetric, then dilute to volume. The Method Blank (MB) consists of 100 mL of reagent water.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

11.3.2 Transfer 100 mL of well-mixed sample or standard to a clean sample digestion bottle. Continue preparation as described under Section 11.4.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

Note: Spiking is done before the addition of acids or reagents.

11.4 Water Bath Protocol – Water Samples

11.4.2 Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 .

11.4.3 Add 15 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 25-mL additional permanganate the color does not persist, sample dilution prior to re-analysis may be required.

Note: The sample dilution resultant from the addition of more than the original aliquot of permanganate solution must be compensated for in the final calculation.

11.4.4 Add 8 mL of potassium persulfate solution, cover, and heat for two hours in a water bath at 90 - 95 °C.

11.4.5 Cool samples.

11.4.6 Add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.5 Sample Analysis

11.5.1 Automated determination. Refer to Appendix C for instrument setup and operation.

11.5.2 Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. The calibration acceptance criteria is listed in Section 10.6. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.5.3 All measurements must fall within the defined calibration range to be valid. Dilute and re-analyze all samples for analytes that exceed the highest calibration standard.

11.5.4 The following analytical sequence is consistent with Methods 7470A, 245.1, and 7471A.

Instrument Calibration

ICV

ICB

CRA if required

Maximum 10 samples

CCV

CCB

Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run

CCV

CCB

Refer to Quality Control Section 9.0 for quality control criteria.

Note: Samples include the Method Blank (MB), Laboratory Control Sample (LCS), Matrix Spike (MS), Matrix Spike Duplicate (MSD), duplicate, field samples and sample dilutions.

11.5.5 To facilitate the early identification of QC failures and samples requiring rerun, it is

strongly recommended that sample data be reviewed periodically throughout the run.

- 11.5.6 Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance, and troubleshooting.

11.6 Analytical Documentation

- 11.6.2 Record all analytical information in the laboratory information management system (LIMS), including the analytical data from standards, Method Blanks (MB), Laboratory Control Samples (LCSs), Matrix Spike/Matrix Spike Duplicates (MS/MSDs). Any corrective actions or modifications to the method must be noted in a Non-Conformance Memo (NCM).
- 11.6.3 All standards and reagents are logged into the LIMS standards and reagents module. All standards are assigned a unique number for identification.
- 11.6.4 Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.
- 11.6.5 Sample results and associated QC are entered into LIMs for final technical review.
- 11.6.6 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo.
- 11.6.7 Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP projects.

12. DATA ANALYSIS AND CALCULATIONS

- 12.1 ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{\text{Found(ICV)}}{\text{True(ICV)}} \right)$$

- 12.2 CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{\text{Found(CCV)}}{\text{True(CCV)}} \right)$$

12.3 Matrix spike (MS) recoveries are calculated according to the following equation:

$$\% R = 100 \left(\frac{SSR - SR}{SA} \right)$$

Where:

SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

12.4 The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100 \left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2} \right)} \right]$$

Where:

Matrix Spike (MS) = determined spiked sample concentration

Matrix Spike Duplicate (MSD) = determined matrix spike duplicate concentration

$$RPD = 100 \left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2} \right)} \right]$$

Where:

DU1 = Sample result

DU2 = Sample duplicate result

12.5 The final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

$$mg/kg, dry weight = (C \times V \times D) / (W \times S)$$

Where:

C = Concentration (ug/L) from instrument readout

V = Volume of digestate (L)

D = Instrument dilution factor

W = Weight in g of wet sample digested

$$S = \text{Percent solids}/100$$

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the “S” factor must be omitted from the above equation.

- 12.6 The final concentration for an aqueous sample is calculated as follows:

$$mg/L = C \times D$$

Where:

C = Concentration (mg/L) from instrument readout

D = Instrument dilution factor

- 12.7 The Laboratory Control Sample (LCS) percent recovery is calculated according to the following equation:

$$\%R = 100 \left(\frac{\text{Found}(LCS)}{\text{True}(LCS)} \right)$$

- 12.8 Appropriate factors must be applied to sample values if dilutions are performed.
- 12.9 Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

- 13.1 Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.1.

13.2 Training Qualification

- 13.2.1 The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14 POLLUTION PREVENTION

- 14.1 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”.

15 WASTE MANAGEMENT

15.1 All waste must be disposed of in accordance with Federal, State, and Local laws and 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 Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for “Waste Management and Pollution Prevention.”

15.2 Waste Streams Produced by this Method

15.2.1 The following waste streams are generated by this method.

15.2.1.1 Acid Waste. This waste disposed of in the designated container labeled “Acid Waste”.

15.2.1.2 Acid waste-aqueous waste generated by the analysis. Samples are disposed of in the acid waste drum located in the Metals lab. The contents of the drum are neutralized and released to the POTW.

16. REFERENCES

16.1 References

16.1.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury)

16.1.2 “Methods for the Chemical Analysis of Water and Wastes”, Rev. 3.0 (1994)

16.1.3 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury)

16.1.4 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Revision 2, February 2007, Method 7471B (Mercury)

16.1.5 [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version

16.1.6 TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version

16.1.7 [Corporate Quality Management Plan \(CQMP\)](#), current version

16.1.8 Revision History

Historical File:	Revision 1.1: 04/17/97	(NC-MT-011) Revision 0: 12/12/07
(formerly CORP-MT-0007NC)	Revision 2.2: 02/06/01	(NC-MT-011 Rev 1 & NC-MT-013 Rev 0): 01/07/09
	Revision 2.3: 05/15/01	Revision 0: 09/27/10
	Revision 2.4: 10/28/02	Revision 1-A: 04/17/12
	Revision 2.5: 11/22/04	

16.2 Associated SOPs and Policies, current version

16.2.1. QA Policy, [QA-003](#)

16.2.2. Glassware Washing, [NC-QA-014](#)

16.2.3. Statistical Evaluation of Data and Development of Control Charts,
[NC-QA-018](#)

16.2.4. Method Detection Limits and Instrument Detection Limits, [NC-QA-021](#)
and [CA-Q-S-006](#)

16.2.5. Supplemental Practices for DoD Project Work, [NC-QA-016](#)

16.2.6. Standards and Reagents, [NC-QA-017](#)

16.2.7. Calibration Curves (General), [CA-Q-S-005](#)

16.2.8 Section of Calibration Points, [CA-T-P-002](#)

16.2.9 Subsampling, [NC-IP-001](#)

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1 Modifications/Interpretations from Reference Method

17.1.1 Modifications from Method 7471A

17.1.1.1 Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP

requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

- 17.1.1.2 Chapter 1 of SW-846 states that the method blank must not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2 Modifications from both Methods 7470A and 245.1

- 17.1.2.1 The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.
- 17.1.2.2 This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, “Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology.”

17.1.3 Modifications from Method 7470A

- 17.1.3.1 Chapter 1 of SW-846 states that the method blank must not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit if the samples associated with the method blank are equal to or above the reporting limit.

17.1.4 Modifications from Method 245.1

- 17.1.4.1 Method 245.1 states that standards are not heated. TestAmerica North Canton prepares heated standards for this method.
- 17.1.4.2 Stannous Chloride is prepared in hydrochloric acid, instead of sulfuric acid, per instrument manufacturer recommendations.
- 17.1.4.3 Section 9.3.4 of the method states that the CCB must be less than the MDL. The laboratory uses the criteria that the CCB result must fall within \pm RL from zero.

APPENDIX A - TABLES

**TABLE I. MERCURY REPORTING LIMITS, CALIBRATION STANDARD,
QC STANDARD AND SPIKING LEVELS**

Soil RL (mg/kg)	0.1
Standard Aqueous RL (mg/L)	0.0002
TCLP RL (mg/L)	0.002
Std 0 (mg/L)	0
Std 1/CRA (mg/L)	0.0002
Std 2 (mg/L)	0.0005
Std 3 (mg/L)	0.001
Std 4 (mg/L)	0.005
Std 5 (mg/L)	0.010
ICV (mg/L)	0.0025
CCV/Laboratory Control Sample (LCS) (mg/L)	0.005
Matrix Spike (MS) (mg/L)	0.001
TCLP Matrix Spike (MS)	0.005

APPENDIX B - CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas should be kept scrupulously clean.

Powdered Gloves should not be used in the metals laboratory since the powder contains zinc, as well as other metallic analytes. Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX C – INSTRUMENT SETUP

Hg Analysis (Leeman PS200II) System Initialization and Warmup To Set Up Instrument for Analysis

1. F1 Menu
2. Autosampler
 - A. Rack Entry
 - B. Edit (ex. Rack 1), Enter
 - C. Cup ID - Enter (clears sample #'s)
 - E. Press Insert Key and move cursor with arrows to cup ID and begin typing labels.
3. Press F2 Macro key and type in – Hg
 - A. Enter folder name - ex., HG0306, Enter. If folder does not exist, type Y - Enter.
 - B. Type in: “Rack 1”, “Rack 2” etc., Enter.
 - C. Type in: FROM CUP TO CUP

Ex. = 1 30

Do the same for Position 2 if needed. If not needed, you must press “Enter” three times to begin analysis.

Hg Analysis (HYDRA AA)

Instrument Instruction

H4 Analysis

There are 3 separate screens to use--WinHgRunner, WinHgDatabase, and Rack Editor

(Turn on Hg lamp prior to analysis)

1. To Set your Protocol and Dataset

WinHgDatabase – Select a previous protocol, then Save Protocol. Type in file name (ex.: HG40101), then select the (RN) key. This will take you to the WinHgRunner screen.

WinHgRunner – File, New, type in dataset name (ex.: 0101A). Type in batch name (ex.: Water or Solid). Go back to WinHgDatabase to locate the new protocol.

2. Typing Labels

Rack Editor - File, New (pick 44 rack). Type in labels under sample ID, and Save As (ex.: 0101A).

3. Activate Gas and Pump

WinHgRunner – under Control tab, turn on Gas and pump, and pour calibration standards.

4. To Calibrate Curve

WinHgRunner – under Standard tab, select S1 S2 S3 S4 S5 S6 Rep1. To begin analyzing, select Stnd Auto tab.

5. To Check Calibration Curve

WinHgDatabase – under Cal Curve tab linear range >0.995, then accept curve.

6. Verification Standards

WinHgRunner – under the Standard tab, select C1 (ICV) C2 (ICB) C3 (CRA). To begin analysis, select Ck Std Auto tab.

7. Checking Verification Standards:

WinHgRunner – Select the Report Tab to review results.

8. To Begin Analyzing Sample with CCV and CCB:

WinHgRunner – under Standard tab, select C4 (CCB) and C5 (CCV).

WinHgRunner – under Sample tab, type in rack name, start cup, end cup, cups per rack (44). To start analysis, select the Run Auto tab.

9. View Results

WinHgRunner – Select the Report tab.

PRINTING REPORTS

1. To Print Cal Curve

WinHgDatabase – under Cal Curve tab, select Print Cal to print curve.

2. To Print Report

WinHgDatabase – under Report tab under Format, turn on Report. Then select Generate to print.

3. To Transfer Run

For instrument H1

- Hit F4 to bring up the report menu
- Type hotkey 'K' to select a disk to write the run to, then type "A:/name-of-run"
- Ex/ for the first run on Nov 7th, type "A:/hg11107A"
- Type hotkey 'L' to select the .prn file type
- Type hotkey 'G' to generate the file (i.e. write the run to the floppy disk)

Walk the floppy disk to instrument H4's computer, locate the run on the disk, right-click it, and select "Send to→TALSImportH1"

For instrument h4

- **WinHgDatabase** – under Report tab under Format, turn on PRN file and type in file (ex. N:/Inorganics/M1109/name-of-run) where "M1109" is the year and month of the current run. For this example "M1109" is Sept. 2011
- Locate the run that was just saved on the N: drive, right-click it, and select "Send to→TALSImportH4"

Title: FLASHPOINT CLOSED CUP

[Method: SW846 Method 1010 and ASTM D93-08]

Approvals (Signature/Date):


Techology Specialist 04/03/12
Date


Health & Safety Coordinator 04/04/12
Date


Quality Assurance Manager 04/03/12
Date


Laboratory Director 04/03/12
Date

This SOP was previously identified as SOP No. NC-WC-0034, Rev 1.2, dated 09/18/09

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Flashpoint by Pensky-Martens closed cup tester in a variety of wastes, liquids, and solids. It is based on ASTM D93-08 and SW846 Method 1010. Although the approximate working range is 20-200 °F, the test is generally considered complete when the temperature reaches 180°F without a measurable Flashpoint.
- 1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

- 2.1. The sample is heated at a slow constant rate with continual stirring if it is a liquid or water. A small test element is directed into the sample cup at regular intervals. The Flashpoint is the lowest temperature at which the test element causes the vapor above the sample to ignite.

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

- 4.1. Not Applicable

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.
- 5.2. 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
p-Xylene	Flammable	100 ppm-	Inhalation of vapors may be irritating to the nose

	Irritant	TWA	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 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves **MUST** be worn when doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to a Laboratory Supervisor and the EH&S Coordinator.
- 5.9. 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. After the apparatus has cooled the sample may be removed.

- 5.10. **When testing a sample, the analyst shall remain within eyesight of the flash point tester and will manually shut down the tester if it fails to automatically shut down following ignition.**

6. EQUIPMENT AND SUPPLIES

- 6.1. Ignitor and detector
- 6.2. Pensky-Martens closed cup tester with stirrer, stirring motor, internal barometer, and thermocouple
- 6.3. Flash point sample cup with lid

7. REAGENTS AND STANDARDS

- 7.1. Reagents
 - 7.1.1. p-Xylene

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Samples are not chemically preserved.
- 8.2. Samples are stored in glass containers at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. Samples are not to be stored in plastic containers since volatile materials may diffuse through the walls of the enclosure.

9. QUALITY CONTROL

- 9.1. Batch Definition
 - 9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS and Method Blank) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24 hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.
- 9.2. Laboratory Control Sample (LCS)

9.2.1 One LCS must be processed with each analytical batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process and the accuracy of the Flashpoint Apparatus. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.2.2 One LCS consisting of p-Xylene will be analyzed at the beginning of every batch. P-Xylene has a flashpoint of 81 °F. If the flashpoint of the p-Xylene varies by more than ± 2 °F, corrective action is required before samples can be analyzed.

NOTE: Dependant upon ambient temperature, p_Xylene may have to be cooled to just above the freezing point in order to achieve accurate results.

9.2.3 Corrective Action for LCS

9.2.3.1 If the p-Xylene flashpoint temperature is outside of established control limits, the system is out of control and corrective action must occur.

9.2.3.2 Corrective action consists of troubleshooting the apparatus for errors and cleanliness, followed by re-analysis of the p-Xylene LCS.

9.3. Duplicates

9.3.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

9.3.2. Sample duplicates are performed at a minimum frequency of 10% per matrix (or one per analytical batch) and must meet laboratory-specific limits for precision. Soil and Waste matrices may be combined for batching purposes.

9.4. Control Limits

9.4.1. For this test method, the RPD value is used to assess the sample duplicate.

9.5. Nonconformance and Corrective Action

9.5.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration of tester

10.1.1. Determine the flash point of p-Xylene following the procedures outlined in Section 11.3.

10.1.2. The tester is operating properly when a value of $81 \pm 2^{\circ}\text{F}$ is obtained (See section 9.2).

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Non-Conformance Memo. The Non-Conformance Memo shall be filed in the project file in LIMS.

11.2. Sample Preparation Procedure

11.2.1. Not Applicable

11.3. Sample Analysis Procedure

11.3.1. Operate the Pensky-Martens tester according to the manufacturer's specifications, in a well-ventilated area away from flammable materials and significant air movement. Operating manuals are located in the laboratory near the tester. Performing this analysis under a hood is the best approach - ensure that the air intake and hood lights are turned off. Inspect the igniter coil closely to ensure the filaments are not touching. Proper placement of the igniter coil in the flashpoint apparatus is crucial to achieving accurate results. Fill the sample cup to the designated line with sample, and assemble the tester as directed.

11.3.1.1. Solid samples require a modified cover for the sample cup. The solid material is placed in the cup until even with the designated line. The sample is not stirred.

11.3.2. A flash check (LCS) must be analyzed with each analytical batch of samples. The compound p-Xylene is used to provide the analyst a reference true flash. The flash temperature is recorded in LIMS. - The true flash temperature for p-Xylene is 81°F . The acceptable range for p-Xylene flashpoint is 79 to 83°F . If the p-Xylene flashpoint is outside of this range, troubleshoot the system and rerun the p-Xylene. Sample analysis will not proceed until a passing p-Xylene flashpoint is achieved.

11.3.3. Pour the sample into the cup, assemble the apparatus, and record the initial temperature. Start the flashpoint apparatus.

- 11.3.3.1. If sample flashes, record the temperature at which the flash occurred in LIMS. Repeat sample for confirmation using the observed flashpoint as the estimated flashpoint.

NOTE: Confirmation analysis are run using a program that is specifically built for known flashpoints. Reference the apparatus user manual to chose the appropriate program.

- 11.3.3.2. If the temperature reaches 180°F and no flash occurs (see manual), turn off flashpoint and record > 180°F as the flashpoint in LIMS.

NOTE: Some samples require an upper limit flashpoint detection of 200 °F. This will be noted in the method comments. Samples with these limits that do not flash should be reported as > 200 °F

- 11.3.4. If solvents are used to clean sample cups, be sure to clean thoroughly with reagent water to prevent contamination.

NOTE: Some samples may burn, but not flash. If possible, record the initial temperature at which it burns in the comments section of the worksheet.. Report these samples as “DNF” with an NCM.

Some samples have a flashpoint below room temperature. If this is known, the sample should be chilled to just above freezing and then analyzed promptly to confirm a true flashpoint.

11.4. Analytical Documentation

- 11.4.1. Record all analytical information in LIMS including the analytical data from standards and any corrective actions or modifications to the method.
- 11.4.2. All standards are logged into the LIMS standards and reagents module.
- 11.4.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.
- 11.4.4. Sample results and associated QC are entered into the LIMs where a first and second level review will be done.

12. DATA ANALYSIS AND CALCULATIONS

- 12.1. If the sample did not flash, report > 180°F or > 200 °F as requested..

- 12.2. If the sample flashes, record and report the observed flashpoint.

13. METHOD PERFORMANCE

- 13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.
- 13.2. Training Qualifications
- 13.2.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.
- 13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

- 14.1. 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".

15. WASTE MANAGEMENT

- 15.1. Refer to the Laboratory Sample and Waste Disposal plan.
- 15.2. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.
- 15.3. 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 section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".
- 15.4. Waste Streams Produced by the method
- 15.4.1. The following waste streams are produced when this method is carried out.
- 15.4.1.1. **Solid samples.** Solids are put into the red can for the debris waste stream
- 15.4.1.2. **Liquid samples and waste solvents.** Flammable wastes including the Xylene standard are disposed of in the solvent waste stream located in the red can in the hood. Adding water to the solvent waste stream should be avoided.

16. REFERENCES

16.1. References

16.1.1. Annual Book of ASTM Standards, ASTM Method D93-08, Flashpoint by Pensky-Martens Closed Tester

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Pensky-Martens Closed Cup Method for Determining Ignitability, Method 1010

16.1.3. Corporate Quality Management Plan (CQMP), current version

16.1.4. TestAmerica North Canton Quality Assurance Manual (QAM), current version

16.1.5. Revision History

Historical File:		Revision 0: 10/24/97		Revision 1.2: 09/18/09
		Revision 1.0: 09/25/03		
		Revision 1.1: 06/28/07		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-018

16.2.4. Standards and Reagents, NC-QA-017

16.2.5. Supplemental Practices for DoD Project Work, NC-QA-016

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Deviations from Method


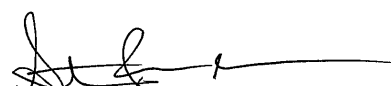


17.1.1. Methods SW846 1010 and ASTM D93-08 do not reference solid materials. Section 11.3.1.1 notes the procedure for solid samples.

17.1.2. ASTM D93-08 section 3.1.3 states that barometric pressure is used in determining the flashpoint. The laboratory uses a flashpoint apparatus that has an internal barometer, which adjusts the flashpoint temperature displayed accordingly.

Title: ANALYSIS OF PESTICIDES AND PCBs

[Method: EPA Method 608]

Approvals (Signature/Date):

 _____ Technology Specialist	<u>05/16/11</u> Date	 _____ Health & Safety Coordinator	<u>05/16/11</u> Date
 _____ Quality Assurance Manager	<u>05/20/11</u> Date	 _____ Laboratory Director	<u>05/18/11</u> Date

This SOP was previously identified as SOP No. NC-GC-007, Rev 4, dated 03/27/09

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of concentrations of pesticides and PCBs (Table 4) in wastewater. It is based on EPA Method 608. The working linear range is highly instrument, column, and compound dependent. Working linear ranges are listed in Table 1. Reporting limits are listed in Table 4.
- 1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

- 2.1. This method provides gas chromatographic conditions for detection and identification of pesticides and PCBs in wastewater.
- 2.2. An aliquot of prepared sample is injected into a gas chromatograph (GC) and pesticide and/or PCB compounds in the extract are detected by an electron capture detector (ECD).

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

- 4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Contamination by carryover may occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a hexane blank to check for cross-contamination.
- 4.3. Sulfur will interfere and can be removed using procedures described in SOP NC-OP-025.
- 4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including Sulfuric Acid Cleanup (Method 3665A) (PCB only) and TBA cleanup (Method 3660B). These cleanup procedures are included in SOP NC-OP-025. Using hexane / acetone as the extraction solvent (rather than hexane / methylene chloride) will reduce the amount of interferences extracted.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.
- 5.2. 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.
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.
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 degrades the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded. Other gloves will be cleaned immediately.
- 5.4. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, and the BHCs. Primary standards of these toxic compounds should be prepared in a hood.

- 5.5. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.
- 5.6. It is recommended that analysts break up work tasks to avoid repetitive motion tasks, such as opening a large number of vials or containers in one time period.
- 5.7. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.8. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.9. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.10. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.11. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.
- 5.12. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.
- 5.13. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

- 6.1. Gas chromatographic system
 - 6.1.1. Gas chromatograph: modified to accept megabore columns
 - 6.1.2. Data system or integrator: capable of peak integration
 - 6.1.3. Gas chromatographic columns are shown in Table 2.
 - 6.1.3.1. Since confirmation runs are required for pesticides and PCBs, a Restek press fit "Y" splitter can be used to allow two columns to be utilized with one autosampler injector.

- 6.1.4. Autosampler: capable of reproducible injections
- 6.1.5. Carrier gas: Hydrogen, ultra high purity (99.999%)
- 6.1.6. Make-up gas: Nitrogen, ultra high purity (99.999%)
- 6.1.7. Detector: electron capture detector (ECD)
- 6.2. Pipettes: disposable, 10 - 20 μ L, 25 - 50 μ L, 100 - 200 μ L Pasteur, 5 3/4 inch
- 6.3. Syringes: gas-tight, 250 μ L, 500 μ L, and 1 mL
- 6.4. Autosampler vials: 1 mL with 11 mm crimp cap, Teflon®/silicon septum liner
- 6.5. Test tubes: 10 x 100 mm culture tubes with Teflon®-lined screw caps
- 6.6. Test tube racks

7. REAGENTS AND STANDARDS

7.1. Reagents

- 7.1.1. Hexane: pesticide residue grade

7.2. Standards

- 7.2.1. The pesticides and PCB standards are purchased from chemical suppliers. Certificates of analysis are supplied with each standard.

7.2.2. Stock Standard Solution

- 7.2.2.1. All individual pesticides and PCBs are prepared in hexane. The solutions are stored per manufacturer's instruction. Stocks are stored for one year

7.2.3. Working Standards

- 7.2.3.1. A series of at least three working standards is prepared in hexane at concentrations that cover the linear range of the instrument. The lowest level must be at, or near, the method reporting limit. These solutions are stored at 4°C \pm 2°C for up to six months. They are replaced sooner if comparisons with laboratory control samples indicate a problem.
- 7.2.4. A system evaluation mix PEM (performance evaluation mix) is prepared in hexane and contains the components shown in Table 3. This mix must be replaced after one year, or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Water samples are stored in glass containers with Teflon®-lined caps at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ until the time of extraction.
- 8.2. Sample extracts and dilutions are stored in test tubes and vials at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ until the time of analysis.
- 8.3. The holding time for pesticide analysis is seven days from sampling to extraction. The holding time for PCB analysis is one year from sampling to extraction.
- 8.4. Extracts and preparative dilutions are analyzed within 40 days of extraction for Pesticide analysis. Extracts are analyzed within one year of extraction for PCB analysis.

9. QUALITY CONTROL

9.1. Batch Definition

- 9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

- 9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

9.2.2. Corrective Action for Blanks

- 9.2.2.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**
- 9.2.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One aqueous LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.3.2. Corrective Action for LCS

9.3.2.1. If a control analyte is outside established control limits the system is out of control and corrective action must occur.

9.3.2.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable.
This must be addressed in the project narrative

9.3.2.3. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable.

9.4. Matrix Spike (MS)

9.4.1. One MS must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. The MS results are used to determine the effect of a matrix on the accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS analysis.

9.4.2. A Matrix Spike sample will be extracted for every ten samples.

9.4.3. Corrective Action for MS

9.4.3.1. If the analyte recovery falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include re-preparation and re-analysis of the batch.

9.4.3.2. If the native analyte concentration in the MS exceeds 4x the spike level for that analyte, the recovery data is reported as DIL (diluted out).

9.4.3.3. If an MS is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed.

9.5. Surrogates

- 9.5.1. Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.
- 9.5.2. Each sample, blank, and QC Sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.
- 9.5.3. Decachlorobiphenyl (DCB) and 2,4,5,6-Tetrachloro-m-xylene (TCMX) are spiked into every method blank, LCS, and matrix spike.
- 9.5.4. If DCB and TCMX surrogate recoveries fail for the method blank, data must be evaluated in the following manner.
 - 9.5.4.1. Check all calculations to ensure that no errors were made; check internal standard (if applicable) and surrogate spiking solution for degradation, contamination, etc.; also check instrument performance.
 - 9.5.4.2. If the above step fails to reveal a problem, re-analyze the blanks and/or samples. If re-analysis does not confirm original results and is within QC acceptance criteria, then the problem was within the analyst's control and only the re-analyzed data should be reported.
 - 9.5.4.3. If the sample with surrogate recoveries outside the recovery limits was a sample used for a MS and the surrogate recoveries in the MS are also outside the control limits, then the sample, and the MS do not require re-analysis as this phenomenon would indicate a possible matrix problem.
 - 9.5.4.4. If the re-analysis does confirm the original results, then the following steps should be taken.
 - 9.5.4.4.1. For a blank, the analytical system must be considered out of control. The problem must be corrected before continuing. This may include recalibration of the instrument.
 - 9.5.4.4.2. For a sample, the results from the original analyses must be reported and the data flagged as surrogates out due to matrix effect
 - 9.5.4.4.3. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

9.6. Control Limits

- 9.6.1. Laboratory control limits are method specified. Control limits are easily accessible via LIMs.

9.7. Method Detection Limits (MDLs) and MDL Checks

9.7.1. MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006

9.7.2. MDLs are easily accessible via LIMs.

9.8. Nonconformance and Corrective Action

9.8.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. If the injection port or front of the column is dirty, 4,4'-DDT and endrin are easily degraded in the injection port. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting 1 µL of the PEM. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 15% replace the glass injection insert with a cleaned and deactivated insert. If this procedure fails to eliminate degradation problem, clip off up to one foot of the injection port side of the column. Calculate the percent breakdown as follows:

$$\%Breakdown\ from\ 4,4'-DDT = \frac{Total\ DDT\ Degradation\ Peak\ Area\ (DDE + DDD)}{Total\ DDT\ Peak\ Area\ (DDT + DDE + DDD)} \times 100$$

$$\%Breakdown\ (Endrin) = \frac{Total\ Endrin\ Degradation\ Peak\ Area\ (Endrin\ Aldehyde + Endrin\ Ketone)}{Total\ Endrin\ Peak\ Area\ (Endrin + Endrin\ Aldehyde + Endrin\ Ketone)} \times 100$$

10.1.2. Analyze calibration standards at a minimum of three concentration levels utilizing the GC conditions in Section 11.5. One of the standards is analyzed at, or near, the concentration which corresponds to the detection limit.

10.1.3. Each calibration standard is injected into the GC with the same technique used to inject the samples (i.e., autosampler injection, manual injection).

- 10.1.4. The calibration factor for each pesticide is calculated as follows (for multi-peak responding components, 3 - 5 peaks are chosen and the corresponding heights or areas are summed).

$$Cf = \frac{\text{Height or Area}}{\text{Weight Injected (ng)}}$$

- 10.1.5. The average calibration factor for each pesticide or PCB is determined using all calibration factors from the initial calibration curve as follows.

$$Cf_{average} = \frac{Cf_1 + Cf_2 + Cf_3}{3}$$

- 10.1.6. The percent relative standard deviation (%RSD) is calculated from the initial calibration as follows.

$$\%RSD = \frac{SD}{Cf_{avg}} \times 100$$

Where:

%RSD = Percent Relative Standard Deviation

SD = Standard Deviation for a small population (On - 1)

CF = Average Calibration Factor

- 10.1.7. If the %RSD is less than 10% over the working range linearity through the origin can be assumed and the average calibration factor may be used in place of a calibration curve.
- 10.1.8. Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted unless an injection or instrument problem confined to that point can be clearly documented as described below. Removal of points for individual analytes from levels other than the highest and lowest is not permitted in any event.
- 10.1.9. If the analyst can document that a level is not valid because of an injection or instrument problem confined to that run, the level may be excluded if the curve still has sufficient levels, or the run may be repeated once only. The whole level (all compounds) must be removed or replaced. The curve is evaluated with the level removed or replaced. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve re-analyzed. Corrective action may include, but is not limited to, instrument maintenance, and/or re-preparation of standards.
- 10.1.10. One of the following conditions must be satisfied to allow 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 external standard methods the average amount of analyte recovered is less than 70% or greater than 130% of the expected value.

10.1.11. The reason for replacing the level **must** be documented in the run log. The fact that the curve passes criteria with the level removed is **not** alone sufficient evidence to document an injection or instrument problem confined to the level.

10.1.12. 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 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.

10.1.13. 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. Data Validation Calculations

10.2.1. The system uses the following quadratic equation:

$$Y = (a_0 + (a_1X) + (a_2X^2))$$

Where:

Y = Amount of analyte ug/mL

X = Area of compound of interest

a₀, A₁, A₂ can be found in the three point

10.3. Continuing Calibration

10.3.1. The continuing calibration curve is verified at the beginning of an analytical sequence by running a mid-range continuing calibration standard.

10.3.2. The continuing calibration CF (calibration factor) for each pesticide and PCB is calculated using the equation in Section 10.1.4.

10.3.3. The percent difference (%D) between the continuing calibration factor and the average calibration is calculated as follows.

$$\%D = \frac{Cf_{avg} - Cf_c}{Cf_{avg}}$$

Where:

%D = Percent Difference

Cf avg = Average Calibration factor from the initial calibration

Cf_c = Calibration factor from the continuing calibration standard

- 10.3.4. All continuing calibrations on the primary or quantitation column can vary by no more than $\pm 15\%$. If these conditions are not met and the system is in optimum working condition, a new initial calibration curve is generated. All samples associated with a failed continuing calibration are not valid and must be re-analyzed by a system that passed criteria.

10.4. Retention Time Windows

- 10.4.1. Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all pesticide standard mixtures and/or PCB standard mixtures throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in retention time windows that are too tight.

- 10.4.2. Calculate the standard deviation of the three absolute retention times for each single component standard. For toxaphene, choose one major peak from the envelope, and calculate the standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

- 10.4.2.1. Plus or minus three times the standard deviation of the absolute retention times for each standard are used to define the retention time window; however, the experience of the analyst weights heavily in the interpretation of chromatograms. For multi-responding products, reference the retention time window, but primarily rely on pattern recognition.

- 10.4.2.2. If the retention time window as calculated above is less than ± 0.05 minutes, use a retention time window appropriate for the analysis and run time. This allows for slight variations in retention times caused by sample matrix.

- 10.4.3. Calculate retention time windows for each standard on each GC column; and whenever a new GC column is installed, flows rates are readjusted or GC conditions are changed. The data must be retained by the laboratory.

11. PROCEDURE

- 11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. The Nonconformance Memo shall be filed in the project file.
- 11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.
- 11.3. Sample Preparation
- 11.3.1. Refer to the Organic Preparation SOPs NC-OP-037 and NC-OP-038.

11.4. Sample Analysis

- 11.4.1. The sample extract may be screened to determine if the level of the pesticides or PCBs exceed the working range of the calibration curve, an appropriate dilution is performed to maintain a level within the initial calibration curve.

11.5. Recommended Instrument Conditions (may vary by instrument and column used)

- 11.5.1. Hydrogen carrier gas flow rate: 5 - 6 mL/minute

- 11.5.2. Nitrogen make-up gas flow rate: 30 - 35 mL/minute

- 11.5.3. GC Conditions – refer to Table 2 for Recommended Instrument Conditions

- 11.5.4. Two columns of dissimilar phase are required (see Section 6.1.3 for column selection).

- 11.5.5. Injection volume: 1 μ L

11.6. Inject 1 μ L of the sample extract or diluted sample into the GC using the same operating conditions and techniques as those used in the calibration of the instrument.

11.7. Analytical Documentation

- 11.7.1. Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCS, MS, and any corrective actions or modifications to the method.

- 11.7.2. All standards are logged into a department standard logbook. All standards are assigned a unique number for identification. Logbooks are reviewed by the supervisor or designee.

- 11.7.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

- 11.7.4. Sample results and associated QC are entered into the LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification

- 12.1.1. Compare the samples chromatographic peak retention times to the retention time windows established for the analyte of interest. For multi-response analytes, rely primarily on pattern recognition.

- 12.1.2. If the retention time for an unknown peak yields a positive match on the primary column, then the secondary or confirmation column must also yield a positive match.
- 12.1.3. If a positive match is not established on both columns, then no pesticides or PCBs of interest are detected in the sample.
- 12.1.4. The higher of the two results is normally reported. The higher result is not always considered better because the higher result is generally higher because of chromatographic interference. The lower result is reported if any of the following two bulleted possibilities are true.
- There is obvious chromatographic interference on the column with the higher result
 - The continuing or bracketing calibration on the column with the higher result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for re-analysis.)
- 12.1.5. If the relative percent difference (RPD) between the response on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

$$RPD = \frac{R_1 - R_2}{\frac{1}{2}(R_1 + R_2)}$$

Where: R = Result

- 12.1.6. Although retention time windows are established to assist the analyst, sound analytical judgment must also be used while interpreting chromatograms. The experience of the analyst is critical to properly identify pesticides and/or PCBs.

12.1.7. Identification of Aroclors

Retention time windows are used for identification of Aroclors, but the “fingerprint” produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst’s judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

A clearly identifiable Aroclor pattern serves as confirmation of single column GC analysis. Dual column confirmation may be used for specific program requirements or by client request.

12.2. Sample Quantification

12.2.1. The calibration factor of the continuing calibration standard run immediately prior to the sample is used to quantify the pesticides and PCBs. If samples are run immediately after the initial calibration, then the average calibration factor is used. Alternatively, if the continuing calibration meets criteria, the average calibration factor from the original curve may be used for quantitation.

12.2.2. Calculate the weight of the analyte present in the sample as follows.

$$\text{Amount} = \frac{Ht}{Cf}$$

Where:

Amt = Weight of analyte present in the sample
 Ht = Height or area of the analyte present in the sample
 Cf = Calibration factor of the analyte of interest

12.2.3. If the weight (ng) of the analyte present in the sample exceeds the working range of the calibration curve, an appropriate dilution is performed and the sample is re-analyzed. All dilutions are prepared with hexane as the diluent.

12.2.4. Calculate the sample results as follows.

$$\text{Concentration, Pest} = \frac{Ht \times V_f}{V_i \times Cf \times INJ_v} \times D$$

Where:

Ht = Height or area of the analyte present in the sample
 V_f = Final extract volume
 V_i = Initial extraction sample volume or weight
 Cf = Calibration factor
 INJ_v = Injection Volume
 D = Dilution factor, if appropriate (Example: If a 1:10 dilution was performed on the sample, D = 10)

12.2.5. Concentration unit determinations are derived as follows.

$$\text{Concentration, Pest} = \frac{Ht \text{ (Height)} \times V_f \text{ (mL)} \times D \text{ (unitless)}}{V_i \text{ (L)} \times Cf \frac{\text{height}}{\text{ng}} \times INJ_v \text{ (}\mu\text{L)}}$$

12.3. Quantitation of Aroclors

12.3.1. Use 3-5 major peaks or total area for quantitation

12.3.2. If the analyst believes that a combination of Aroclor 1254 and 1260, or a combination of 1242, 1248 and 1232 is present, then only the predominant Aroclor is quantitated and reported; but the suspicion of multiple Aroclors is discussed in the narrative. If well separated Aroclor patterns are present, and then both Aroclors are quantitated and reported.

12.3.3. Second column confirmation of Aroclors will only be performed when requested by the client. The appearance of the multiple peaks in the sample usually serves as a confirmation of Aroclor presence.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. 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".

15. WASTE MANAGEMENT

15.1. 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 Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

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

15.2.1.1. Vials containing sample extracts: These vials are placed in waste containers located in the GC/MS laboratory and identified as "PCB Vial Waste".

15.2.1.2. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCB's must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB and PCB vial waste. Solid PCB waste is placed in containers labeled "PCB Solids Waste". Liquid PCB waste is placed in containers labeled "PCB Liquids Waste". PCB vials are placed in containers labeled "PCB Vial Waste". PCB containing samples are located through a LIMS query and disposed of as PCB containing.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. EPA 600, Methods for Chemical Analysis of Water and Wastes, Method 608

16.1.2. [Corporate Quality Management Plan \(CQMP\)](#), current version

16.1.3. [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version

16.1.4. TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version

16.1.5 Revision History

Historical File:		Revision 0: 09/18/95		
		Revision 1: 06/12/03		
		Revision 2: 11/15/04		
		Revision 3: 02/27/07		
		Revision 4: 03/27/09		

16.2. Associated SOPs and Policies, current version

16.2.1. Continuous Liquid/Liquid Extraction of Organic Compounds from Waters Based on Method SW846 3520C and 600 Series and Waste Dilution Based on Method 3580A, [NC-OP-037](#)

16.2.2. Separatory Funnel Extraction of Organic Compounds from Waters Based on Method SW846 3510C and 600 Series and Waste Dilution Based on Method 3580A, [NC-OP-038](#)

16.2.3. QA Policy, [QA-003](#)

16.2.4. Glassware Washing, [NC-QA-014](#)

16.2.5. Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)

16.2.6. Method Detection Limits and Instrument Detection Limits, [NC-QA-021](#) and [CA-Q-S-006](#)

16.2.7. Standards and Reagents, [NC-QA-017](#)

16.2.8. Cleanup Procedure for Organic Extractable Samples, [NC-OP-025](#)

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. See Table 4

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

Table 1: Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6²
Individual Mix AB						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Methoxychlor	5	10	25	50	100	200
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
β-BHC	5	10	25	50	100	200
δ-BHC	5	10	25	50	100	200
α-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
Multi-Component Standards						
Chlordane (Technical)	20	50	100	200	500	
Toxaphene	200	500	1000	2000	5000	
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200
Aroclor 1016/1260	50	100	200	500	1000	2000
Aroclor 1242	50	100	200	500	1000	2000
Aroclor 1221/1254	50	100	200	500	1000	2000
Aroclor 1232	50	100	200	500	1000	2000
Aroclor 1248	50	100	200	500	1000	2000

Table 2: Instrument Conditions

Parameter	Recommended Conditions
Injection port temp	225°C
Detector temp	300°C
Temperature program	110°C for 1 min, 12°C/min to 220°C to 290°C, 2 min hold
Column 1	RTX-CLPesticides 30m x 0.53mm id, 0.5µm
Column 2	RTX-CLPesticides II 30m x 0.53mm id, 0.25µm
Injection	1 µL
Carrier gas	Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table 3: System Evaluation Mix

Compound
4,4' DDT
Endrin
alpha-BHC
gamma-BHC
beta-BHC
Methoxychlor

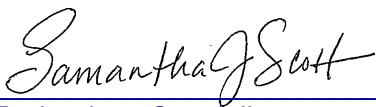
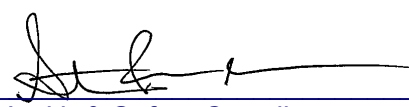
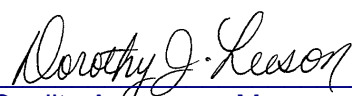
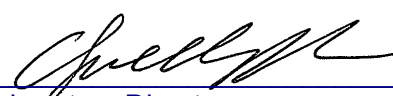
Table 4: Reporting Limits

Common Name	Reporting Limits, µg/L
Aldrin	0.05
α-BHC	0.05
β-BHC	0.05
δ-BHC	0.05
γ-BHC (Lindane)	0.05
Chlordane (technical)	0.5
4,4'-DDD	0.05
4,4'-DDE	0.05
4,4'-DDT	0.05
Dieldrin	0.05
Endosulfan I	0.05
Endosulfan II	0.05
Endosulfan Sulfate	0.05
Endrin	0.05
Endrin Aldehyde	0.05
Heptachlor	0.05
Heptachlor Epoxide	0.05
Toxaphene	2.0
Aroclor-1016	1.0
Aroclor-1221	1.0
Aroclor-1232	1.0
Aroclor 1242	1.0
Aroclor-1248	1.0
Aroclor-1254	1.0
Aroclor-1260	1.0

Title: PHOSPHORUS: TOTAL, ORTHO, AND ORGANIC

[Method: EPA Methods 365.1 and SM 4500-P-E]

Approvals (Signature/Date):

 Technology Specialist	<u>10/14/10</u> Date	 Health & Safety Coordinator	<u>10/05/10</u> Date
 Quality Assurance Manager	<u>10/14/10</u> Date	 Laboratory Director	<u>10/05/10</u> Date

This SOP was previously identified as SOP NC-WC-050, Rev 2.7, dated 06/20/08

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1. SCOPE AND APPLICATION

- 1.1. This method covers the determination of various forms of Phosphorus in drinking, surface, and saline waters, domestic and industrial wastewaters, and a variety of solid matrices. It is based on EPA Method 365.1 and Standard Method 4500-P-E. The working linear range is 0.1 to 1.0 mg/L for waters and 10 to 100 mg/kg for soils.
- 1.2. Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus as determined by calculation.
- 1.3. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

- 2.1. Ammonium molybdate and antimony potassium tartrate react in an acid medium with Phosphorus to form a blue-colored complex which is analyzed photometrically.

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

- 4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Clean all glassware in non-phosphate type detergent followed by several rinses of 1:1 hydrochloric acid (HCl) and reagent water. Refer to the laboratory Glassware Washing SOP (NC-QA-014), current version
- 4.3. Use unpowdered gloves. The silica in powder can interfere.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

- 5.2. 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.
Isopropanol	Flammable	400 ppm-TWA	Flammable liquid and vapor. Harmful if swallowed or inhaled. Causes irritation to eyes and respiratory tract. Affects central nervous system. May be harmful if absorbed through skin. May cause irritation to skin.
Ammonium Persulfate (Peroxydisulfate)	Oxidizer Corrosive	5 mg/m ³ -TWA as Persulfates	Causes irritation to the mucous membranes. Symptoms may include sore throat, shortness of breath, inflammation of nasal passages, coughing, and wheezing. Causes severe irritation or burns to the skin and eyes. Symptoms include redness, itching, pain and burns. Can cause eye damage.
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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

- 5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. All samples with stickers that read “Caution/Use Hood!” **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Spectrophotometer and 1 cm cells
- 6.2. Graduated cylinders: Various
- 6.3. 125 mL (4 oz) Snap-Seal® containers
- 6.4. Erlenmeyer flasks: Various
- 6.5. Volumetric flasks and stoppers: Various
- 6.6. Volumetric and graduated pipettes: Various
- 6.7. Funnels and Whatman #4 filter paper
- 6.8. Boiling beads
- 6.9. pH Meter: Accurate to ± 0.05 units at 25°C
- 6.10. Analytical Balance: Capable of accurately weighing ± 0.0001
- 6.11. Digestion block and digestion tubes.
- 6.12. pH paper
- 6.13. Scientific calculator
- 6.14. 150 mL plastic beakers

- 6.15. Amber glass bottles
- 6.16. Disposable test tubes
- 6.17. Konelab auto-analyzer / disposable cuvettes

7. REAGENTS AND STANDARDS

7.1. Reagents

- 7.1.1. Sulfuric Acid (H_2SO_4), Concentrated: Reagent grade
- 7.1.2. Hydrochloric Acid, (HCl), Concentrated: Reagent grade
- 7.1.3. Hydrochloric Acid, $\text{HCl}(1:1)$: Carefully add 250 mL of concentrated hydrochloric acid to 250 mL of reagent water. Store in a well-labeled bottle.
- 7.1.4. 5 N Sulfuric Acid, H_2SO_4 : Carefully add 70 mL of concentrated sulfuric acid to 400 mL of reagent water. Dilute to 500 mL with reagent water.
- 7.1.5. Sodium Hydroxide: Reagent grade
- 7.1.6. 6 N Sodium Hydroxide, NaOH : Add 120 g of sodium hydroxide pellets to 400 mL of reagent water and mix. Dilute to 500 mL using reagent water.
- 7.1.7. Phenolphthalein: Reagent grade
- 7.1.8. Isopropyl Alcohol: Reagent grade
- 7.1.9. Phenolphthalein Indicator: Add 0.5 g phenolphthalein to 50 mL of Isopropyl alcohol and mix. Add 50 mL of reagent water and mix.
- 7.1.10. Ascorbic Acid: Reagent grade
- 7.1.11. Ascorbic Acid Solution: Add 1.76 g of ascorbic acid to a 100 mL volumetric flask and dilute to volume with reagent water. Make daily.
- 7.1.12. Antimony Potassium: Reagent grade
- 7.1.13. Antimony Potassium Tartrate Solution, $\text{K}[\text{SbO}]\text{C}_4\bullet\frac{1}{2}\text{H}_2\text{O}$: Add 1.37 g antimony potassium to a 500 mL volumetric flask and bring to volume with reagent water. Store in an amber glass bottle at $4^\circ\text{C} \pm 2^\circ\text{C}$.
- 7.1.14. Ammonium Molybdate: Reagent grade

- 7.1.15. Ammonium Molybdate Solution, $[\text{NH}_4]_6\text{MO}_7 \text{O}_{24} \cdot 4\text{H}_2\text{O}$: Add 20 g ammonium molybdate to a 500 mL volumetric flask and dilute to volume with reagent water. Store in a plastic bottle at $4^\circ\text{C} \pm 2^\circ\text{C}$.
- 7.1.16. Combined Reagent: For 100 mL, mix 50 mL 5 N H_2SO_4 , 5 mL antimony potassium tartrate solution, 15 mL ammonium molybdate solution, and 30 mL ascorbic acid solution in a 500 mL Erlenmeyer flask. Mix after addition of each reagent. Let all reagents reach room temperature before they are used and mix in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until turbidity disappears. Stable up to four hours.
- 7.1.17. Ammonium Persulfate (Peroxydisulfate): Crystals, $(\text{NH}_4)_2 \text{S}_2 \text{O}_8$, Reagent grade
- 7.1.18. Potassium-dihydrogen Phosphate: Reagent grade
- 7.1.19. Sulfuric Acid Solution, 11 N: Slowly add 310 mL concentrated H_2SO_4 to 600 mL DI water. When cool, dilute to 1 liter.
- 7.1.20. Sodium Hydroxide, 1 N: Dissolve 40g NaOH in 600 mL DI water. Cool and dilute to 1 liter
- 7.2. Standards
- 7.2.1. Primary Stock standard: 1000 mg/L Phosphorus standard
- 7.2.2. Secondary Stock Standard, 50 mg/L: Add 0.2197 pre-dried KH_2PO_4 (Potassium-dihydrogen Phosphate) to a 1000 mL volumetric flask and dilute to volume with reagent water. Stable for three months. Alternatively, a purchased second source may be used.
- 7.2.3. Calibration Standards
- 7.2.3.1. Prepare the following standards by making a 50 ppm stock standard, and pipetting the required volume of the 50 ppm primary standard into 100 mL volumetric flasks. Dilute to volume using reagent water. The low standard must be at, or below, the reporting limit.

Concentration (mg/L)	Pipette (mL)	Stock Conc. (mg/L)	Final Volume (mL)
50	5	1000	100
*1.0	1.0	50	50
*0.75	0.75	50	50
*0.50	0.50	50	50
0.25	0.25	50	50
*0.20	0.20	50	50
*0.10	0.10	50	50
*0	0	0	50

* Calibration Standards

7.2.3.2. Calibration standards must be taken through the sample preparation procedure as described in Section 11.4.

7.2.3.3. Continuing Calibration Verification (CCV) Standard, 0.5 mg/L: Pipette 0.5 mL of the primary 50 mg/L standard into a 50 mL volumetric and dilute to volume with reagent water.

7.2.4. Laboratory Control Sample (LCS) Standard

7.2.4.1. LCS Standard for Total Phosphate, 0.5 mg/L: Pipette 0.5mL of the 50 mg/L secondary standard into a beaker add 50mL of DIH₂O. The true value is 0.5mg/L. A purchased standard may be used as the LCS. The concentration of the purchased standard must be recorded on the analytical logsheet.

7.2.5. LCS Standard for orthophosphate, 0.25 mg/L: Pipette 0.25 mL of the 50 mg/L standard to a 50 mL volumetric flask and dilute to volume with reagent water. A purchased standard may be used for the LCS.

7.2.6. Matrix Spike Standard

7.2.6.1. MS/MSD Standard, 50 mg/L: Prepared from the primary standard (Section 7.2.1) or the secondary standard (Section 7.2.2).

8. SAMPLE COLLECTION, PRESENTATION, AND STORAGE

8.1. Water samples for total Phosphorus are preserved with sulfuric acid to a pH of <2 and stored at 4°C ± 2°C in plastic or glass containers.

- 8.2. Samples for orthophosphates and solids are not chemically preserved and are stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ in plastic or glass containers.
- 8.3. The holding time for Total Phosphorus is 28 days from sampling to analysis.
- 8.4. The holding time for Orthophosphate is 48 hours from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

- 9.1.1. A batch is a group of no greater than 20 samples QC samples (LCS, Method Blank, MS, MSD) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

- 9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.
- 9.2.2. A reagent water blank consisting of 50 mL of reagent water is analyzed with each analytical batch of samples.
- 9.2.3. Corrective Action for Blanks
 - 9.2.3.1. If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample date **must be addressed in the project narrative.**
 - 9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

- 9.3.1. One LCS from an independent source must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for Method 365.1 LCS recoveries are 90% to 110%. LCS recoveries outside of these control limits require corrective action.
- 9.3.2. For Total Phosphorus, a midrange LCS, consisting of either 0.5 mL of the 50 mg/L secondary standard or 50 mL of purchased standard, must be digested and analyzed with each analytical batch of samples.
- 9.3.3. For Orthophosphate, a midrange LCS consisting of 0.25 mL of the 50 mg/L secondary standard must be analyzed with each analytical batch of samples. A commercially available reference solution may be used and is highly recommended.
- 9.3.4. Corrective Action for LCS
 - 9.3.4.1. If any analyte is outside established control limits the system is out of control and corrective action must occur.
 - 9.3.4.2. The only exception is that if the LCS recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**
 - 9.3.4.3. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable. For Ohio VAP samples, re-preparation is required.

9.4. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

- 9.4.1. One MS/MSD pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Criteria for Method 365.1 MS/MSD recoveries are 90% to 110%. Matrix spike recoveries outside of these control limits require corrective action as stated in Section 9.4.4. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific

sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.4.2. For Total Phosphorus, a MS/MSD consisting of 50 mL of sample and 0.5 mL of the 50 mg/L standard will be digested and analyzed with each analytical batch of samples.

9.4.3. For Orthophosphate, a MS/MSD consisting of 50 mL of sample and 0.5 mL of the 50 mg/L standard will be analyzed with each analytical batch of samples.

9.4.4. Corrective Action for MS/MSDs

9.4.4.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include re-preparation and re-analysis of the batch.

9.4.4.2. If the native analyte concentration in the MS/MSD exceeds 4x the spike level for that analyte, the recovery data is reported as "amount" MSB. The Exception Code is changed to NC. The following two footnotes will appear on the report page "NC The recovery and/or RPD were not calculated." "MSB The recovery and RPD were not calculated because the sample amount was greater than four times the spike amount."

9.4.4.3. If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to laboratory RPD limits.

9.5. QC Acceptance Criteria

9.5.1. Control limits are established by the laboratory as described in NC-QA-018. Method 365.1 requires $\pm 10\%$ recoveries on all LCSs and MS/MSD pairs.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits easily accessible via LIMs (QC Browser Program).

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.6.2. MDLs are easily accessible via LIMs (QC Browser Program).

9.7. Nonconformance and Corrective Action

- 9.7.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

10.1.1. Konelab

- 10.1.1.1. Follow instrument startup and calibration procedures according to the manufacturer's manual.

10.2. Continuing Calibration

- 10.2.1. The run is checked every ten samples and at the end of the run using a midrange CCV to verify continued linearity. It cannot vary from the original curve by more than $\pm 10\%$ or recalibration is required.
- 10.2.2. System cleanliness is checked every ten samples and at the end of the run using a CCB. It cannot contain the analyte of interest above the reporting limit or recalibration is required.

11. PROCEDURE

- 11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. The Nonconformance Memo shall be filed in the project file.
- 11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.
- 11.3. Sample Preparation
- 11.3.1. Summary
- 11.3.1.1. Total Phosphorus is digested to yield Orthophosphate using sulfuric acid and ammonium persulfate.
- 11.3.1.2. This test is easily contaminated due to soaps and Phosphorus containing chemicals. Be sure all glassware is thoroughly washed with phosphate free soap and rinsed with 1:1 HCl prior to use.

11.4. Sample Preparation Procedure

11.4.1. Orthophosphate

- 11.4.1.1. For waters, adjust the pH of the sample to 7 (\pm 0.2) with 1 N NaOH or 11 N H₂SO₄ using a pH meter or narrow range pH paper; and filter the sample, if necessary, due to large amounts of suspended solids.
- 11.4.1.2. For solids, follow the extraction procedure in SOP NC-IP-009.

11.4.2. Total Phosphorus

- 11.4.2.1. Transfer 50 mL (or aliquots brought up to 50 mL) of sample to a digestion tube. For solid samples, use 0.5 g of sample in 50 mL of reagent water.
- 11.4.2.2. Add 3 - 5 boiling beads to each flask.
- 11.4.2.3. Add 1 mL of 11 N H₂ SO₄ and mix.
- 11.4.2.4. Add 0.4 g Ammonium Persulfate (Peroxydisulfate) and mix.
- 11.4.2.5. Place the tube in the digestion block and heat to boiling. Set the digestion block at 160°C.
- 11.4.2.6. Shut off the heater when the sample boils down to near dryness and white fumes are liberated. Sample volume should be 10 mL.

NOTE: If the sample turns brown or black during digestion, a dilution and redigestion is necessary.

NOTE: Do not allow the sample to go to dryness. Dryness will require the reprep and re-analysis.
- 11.4.2.7. Allow the sample to cool.
- 11.4.2.8. Add two drops of phenolphthalein indicator.
- 11.4.2.9. Add 6 N NaOH until a pink color develops and remains. pH should be >9. If the digestate turns pink and then goes clear, check the pH with pH paper to ensure it is >9. Add more NaOH if necessary. The pH is critical to color development.
- 11.4.2.10. Add 5 N H₂SO₄ dropwise until clear. Bring the volume up to 50 mL with reagent water.

11.4.2.11. If the sample is not clear at this point, syringe filter before analysis on the Konelab.

NOTE: For Dissolved Phosphorus Species, the sample must be filtered during sampling or prior to preservation and/or analysis.

11.5. Preparation Documentation

11.5.1. All necessary information is recorded on the Total Phosphorous Digestion analytical logsheet.

11.6. Sample Analysis

11.6.1. Summary

11.6.1.1. The combined reagent is added to an aliquot of sample forming a blue complex upon the presence of Orthophosphate. The sample is analyzed on the spectrophotometer at 880 nm or on the Konelab autoanalyzer.

11.7. Sample Analysis Procedure (Total Phosphorus and Orthophosphate)

11.7.1. Sample Analysis using the Konelab Autoanalyzer

11.7.1.1. Add the necessary reagents to the Konelab reagent “wheel.”

11.7.1.2. Insert samples into the autoanalyzer segments.

11.7.1.3. Start the appropriate method on the Konelab autoanalyzer.

11.8. Analytical Documentation

11.8.1. Record all analytical information on the analytical logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method. The printout from the Konelab may also be used.

11.8.2. All standards are logged onto the departmental standard logsheet. All standards are assigned a unique number for identification. Logbooks are reviewed by the supervisor or designee.

11.8.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.8.4. Sample results and associated QC are entered into LIMs after final technical review.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calculations

$$12.1.1. \text{Concentration, mg/L} = \frac{\text{Absorbance} - A}{B}$$

Where:

A = Y-intercept (from 10.1.2)

B = Slope (from 10.1.2)

$$12.1.2. \text{Orthophosphate, mg/L or mg/kg} = \text{Concentration} \times D$$

Where:

$$D = \text{Dilution factor} \left(\frac{\text{total volume analyzed}}{\text{sample volume used}} \right)$$

NOTE: For solids with extraction procedure, $D = 10 \left(\frac{100 \text{ mL}}{10 \text{ g}} \right)$

$$12.1.3. \text{Total Phosphorus, mg/L} = \text{Concentration} \times D$$

For solids, $D = 100 \left(\frac{50 \text{ mL}}{0.5 \text{ g}} \right)$; therefore,

$$\text{Concentration, mg/kg} = \text{Concentration, mg/L} \times 100$$

$$12.1.4. \text{LCS \% Recovery} = \frac{\text{Concentration, mg/L}}{\text{True}} \times 100$$

Where:

True = 0.25 (ortho) or 0.5 (total)

$$12.1.5. \text{MS/MSD \% Recovery} = \frac{E - F}{G} \times 100$$

Where:

E = MS/MSD concentration

F = Sample concentration

G = True spike, 0.5 mg/L

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the Laboratory QA files.

14. POLLUTION PREVENTION

14.1. 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".

15. WASTE MANAGEMENT

15.1. 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 Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

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

15.2.1.1. Acidic sample waste generated by the analysis. Aqueous waste can be poured down the drain if the pH is between 5 and 10. Any sample waste generated that is not in this pH range is collected in a designated container identified as "Acid Waste".

- 15.2.1.2. Contaminated disposable glass or plastic materials utilized in the analysis. Solid materials (gloves, soiled paper products, etc.) are placed in container identified as “Solid Waste”. Do not put liquids in the solid waste container.
- 15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica North Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16. REFERENCES

16.1. References

- 16.1.1. EPA 600, Methods for Chemical Analysis of Water and Wastes, Determination of Phosphorus by Semi-Automated Colorimetry, Method 365.1, Revision 2.0, August 1993
- 16.1.2. Standard Methods for the Examination of Water and Wastewater, 18th Edition, Phosphorus, Methods 4500-P-B & E
- 16.1.3. [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version
- 16.1.4. TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version
- 16.1.5. [Corporate Quality Management Plan \(CQMP\)](#), current version
- 16.1.6. Revision History

Historical File:		Revision 2.1: 07/14/98		Revision 2.7: 06/20/08
		Revision 2.2: 03/09/99		
		Revision 2.3: 02/20/01		
		Revision 2.4: 05/15/01		
		Revision 2.5: 02/07/03		
		Revision 2.6: 11/04/04		

16.2. Associated SOPs and Policies, current version

- 16.2.1. Glassware Washing SOP, [NC-QA-014](#)
- 16.2.2. DI Leachate Procedure for Solids, [NC-IP-009](#)

- 16.2.3. Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)
- 16.2.4. QA Policy, [QA-003](#)
- 16.2.5. Method Detection Limits and Instrument Detection Limits, [NC-QA-021](#) and [CA-Q-S-006](#)
- 16.2.6. Supplemental Practices for DoD Project Work, [NC-QA-016](#)
- 16.2.7. Selection of Calibration Points, [CA-T-P-002](#)
- 16.2.8. Calibration Curves (General), [CA-Q-S-005](#)

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

- 17.1. The lower reporting limit (RL) is 0.1 mg/L for waters and 10 mg/kg for solids.
- 17.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

**Title: TOTAL SOLIDS, PERCENT MOISTURE, AND TOTAL
SETTLEABLE SOLIDS,**

[Method: EPA Methods 160.3 Modified, EPA 160.5, and
ASTM D2216-98 and]

Approvals (Signature/Date):


Technology Specialist 04/18/12
Date


Health & Safety Coordinator 04/19/12
Date


Quality Assurance Manager 04/23/12
Date


Laboratory Director 04/18/12
Date

This SOP was previously identified as SOP No. NC-WC-0004, Rev 3.4, dated 12/22/09

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Total Solids; Percent Moisture; and Settleable Solids; in wastewaters, sludges, and solids. It is based on EPA 160.3 Modified, EPA 160.5, and ASTM D2216-98,. The approximate working range for Total Solids is 10 to 100% for non-waters.
- 1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

- 2.1. A homogenous sample is dried at $104^{\circ}\text{C} \pm 1^{\circ}\text{C}$, and the difference in the weight loss of the sample represents the Total Solids.
- 2.2. Settleable Solids. Settleable matter is measured volumetrically with an Imhoff cone.

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

- 4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Samples high in concentrations of minerals must be dried longer, desiccated, and weighed quickly to prevent any excess weight added due to absorption of water from the atmosphere.
- 4.3. Non-homogeneous samples may give erratic results.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

- 5.2. Oily samples or those that contain volatile chemicals may ignite during this procedure. In the case of a fire, the oven should be turned off and allowed to cool before the sample can be removed and put under a hood.
- 5.3. There are no materials used in this method that have a significant or serious hazard rating. **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.
- 5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut.
- 5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**. Therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Drying Oven
- 6.2. Desiccators
- 6.3. Evaporating dishes: various
- 6.4. Tongue blades
- 6.5. Sample containers

6.6. Top loading balance: capable of accurately weighing ± 0.01 g

6.7. Analytical balance: capable of accurately weighing ± 0.0001 g

6.8. Beakers: glass, various

6.9. Volumetric flasks: various

6.10. Imhoff cones

6.11. Labels

6.12. Graduated Cylinder, 1000 mL, 10mL, Class A

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Reagent water

7.1.2. Sand

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are not chemically preserved.

8.2. Samples are stored in plastic or glass containers at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

8.3. The holding time is 48 hours for settleable solids.

8.4. There is no recommended holding time for non-water samples.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS, Method Blank, sample duplicate) which are processed similarly, with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

- 9.2.1. One method blank (MB) must be processed with each preparation batch of Settleable Solids samples. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit.

NOTE: There is no method blank applicable for Total Solid or Percent Moisture.

9.2.2. Corrective Action for Blanks

- 9.2.2.1.** If the analyte level in the method blank exceeds the reporting limit for the analytes of interest in the sample, all associated samples are re-prepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

- 9.2.2.2.** If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample

- 9.3.1. For the Settleable Solids method, an LCS sample is required.

- 9.3.1.1 One mL of sand will be added to a 10 mL graduated cylinder. 1000 mL of water is added to a liter container. The sand mixture is added to the liter container and mixed. The resulting mixture is transferred to an Imhoff cone and allowed to settle for one hour. Control limits will be 90-110%.

9.4. Duplicates

- 9.4.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.

- 9.4.2. Sample duplicates are performed at a frequency of 10% and must meet laboratory-specific limits for precision.

9.4.3. Sample duplicates are not applicable for Settleable Solids.

9.5. Control Limits

9.5.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.5.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMS.

9.6. Method Detection Limits (MDLs) and MDL Checks

9.6.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.6.2. MDLs are easily accessible via LIMS.

9.7. Nonconformance and Corrective Action

9.7.1. Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Not applicable

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Total Solids (Percent Moisture)

11.3.1. For solid and sludge samples, label and weigh an evaporating dish on an analytical balance. Record the weight in LIMS. For solid samples (TS), a universal tare weight is recorded in LIMS. For solid samples, Sample Receiving will divide the soil sample into a pre-tared container with a label. Weigh and record the wet weight in LIMS.

11.3.2. Sample Duplicate for solid samples (TS), Sample Receiving will supply the sample duplicate. If the sample duplicate is not supplied from Receiving, split some sample off from another container into a new container with a label. Weigh and record the weight in LIMS.

11.3.3. Place dishes with sample in the drying oven (103° - 105°C) until dry (minimum of 12 hours). Document the time samples were placed in the oven in LIMS.

11.3.4. Remove the samples from the drying oven when they are dry. Document the time samples were removed from the oven in LIMS.

11.3.5. Place the dishes in the desiccator for at least one hour. Weigh the sample and dish on the top loading balance. Record the weight in LIMS.

11.4. Percent Moisture

11.4.1. Follow Section 11.3.

11.5. Settleable Solids

11.5.1. A method blank is prepared from one liter of reagent water. A blank must be analyzed with each batch of 20 or less samples to ensure Imhoff cones are clean and free of particulate contamination. An LCS sample must be analyzed as noted in Section 9.3.

11.5.2. Shake one liter of sample vigorously for ten seconds.

11.5.3. Pour the sample into an Imhoff cone, filling the cone to the one-liter mark.

11.5.4. Allow the sample to settle for one hour.

11.5.5. Measure the volume of settleable solids by observing the location of the border between the settled matter and the supernatant liquid.

11.5.5.1. If pockets of liquid are trapped beneath large settled particles, estimate the volume of the pockets and subtract from the total measured volume.

11.6. Analytical Documentation

11.6.1. Record all analytical information in LIMS, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.6.2. All standards are logged into the LIMS standards and reagents module. All standards are assigned a unique number for identification.

11.6.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.6.4. Sample results and associated QC are entered into LIMs. Level I and Level II technical reviews are done in LIMS..

12. DATA ANALYSIS AND CALCULATIONS

12.1. Total Solids

$$\text{Total Solids, \% (non-waters)} = \frac{(A - B) \times 100}{(C - B)}$$

Where: A = Final weight of dried sample and dish, g
B = Initial weight of dish, g
C = Initial weight of wet sample and dish, g

12.2. Dry Weight

$$\text{Dry Weight} = \frac{\text{Sample Test Result} \times 100}{(\%) \text{ Total Solid Results}} = \text{Dry Weight}$$

12.3. Percent Moisture

$$\% \text{Moisture} = 100 - \% \text{TS (Section 12.1)}$$

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. 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".

15. WASTE MANAGEMENT

15.1. 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 Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

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

15.2.1.1. Acidic sample waste generated by the analysis. This waste is collected in the laboratory in a designated container identified as "Acid Waste".

15.2.1.2. Contaminated filter and filter residue generated by the analysis. This waste is collected in the laboratory in a designated container identified as "Solid Waste".

15.2.1.3. Weighing containers and filter residue generated by solid sample analysis. This waste is collected in the laboratory in a designated container identified as "Solid Waste".

- 15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by an annual refresher training.

16. REFERENCES

16.1. References

16.1.1. EPA 600, 1984, Total Residual Solids, Method 160.3

16.1.2. EPA Settleable Solids, Method 160.5

16.1.3. Annual Book of ASTM Standards, Volume 04.08, 1990

16.1.4. [Corporate Quality Management Plan \(CQMP\)](#), current version

16.1.5. [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version

16.1.7. Ohio Bureau of Underground Storage Tank Regulations (BUSTR) Technical Guidance Manual, April 2005

16.1.8. Revision History

Historical File:		Revision 3.0: 08/04/00		Revision 3.3: 09/10/07
		Revision 3.1: 11/06/04		Revision 3.4: 12/22/09
		Revision 3.2: 02/02/06		

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, [QA-003](#)

16.2.2. Glassware Washing, [NC-QA-014](#)

16.2.3. Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)

16.2.4. Method Detection Limits and Instrument Detection Limits, [CA-Q-S-006](#) and [NC-QA-021](#)

16.2.5. Supplemental Practices for DoD Project Work, [NC-QA-016](#)

16.2.6. Standards and Reagents, [NC-QA-017](#)

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)


17.1. Reporting limits

17.1.1. The reporting limit for Method 160.3 is 10%. The reporting limit for Method 160.5 is 0.1 ml/L/hr. The reporting limit for Percent Moisture by ASTM D2216-98 is 0.1%.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

**Title: GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHODS
8000B, 8021B, 8081A, 8081B, 8082, 8082A, 8151A,
615, 8015B, and 8015C**


Approvals (Signature/Date):


Technology Specialist 04/30/11
Date


Health & Safety Coordinator 04/21/11
Date


Quality Assurance Manager 05/01/11
Date


Laboratory Director 04/27/11
Date


Technical Director 04/20/11
Date

This SOP was previously identified as SOP NC-GC-038, Rev 1, Dated 01/15/09

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Table E3	Calibration Levels, Method 8015B and 8015C

1. SCOPE AND APPLICATION

- 1.1. This SOP describes procedures for analysis of organic analytes by Gas Chromatography (GC). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA). The main body of this SOP is based on SW846 Method 8000B. Individual analytes and methods are described in the appendices. See the list of appendices noted in the Table of Contents to determine the appropriate section of the SOP. Reporting limits are listed in each appendix.

2. SUMMARY OF METHOD

- 2.1. In general, semivolatile analytes in aqueous samples are prepared for analysis using continuous or separatory funnel liquid / liquid extraction (SOP NC-OP-037 and NC-OP-038). Solid samples are prepared using sonication or soxhlet (SOP NC-OP-039 and NC-OP-040). Volatile analytes are prepared for analysis using purge and trap methodology (Appendix A).
- 2.2. After the initial preparation step, the sample is introduced to the GC and concentrations of target analytes are measured by the detector response within a defined retention time window, relative to the response to standard concentrations. Internal or external standardization procedures are used as specified in the method appendices.

3. DEFINITIONS

- 3.1. Refer to the TestAmerica North Canton Quality Assurance Manual (QAM), current version, for definitions of terms and acronyms used in this document.

4. INTERFERENCES

- 4.1. Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. In particular, this is a problem with non-selective detectors such as the Flame Ionization Detector (FID). See Appendices A through E for interferences specific to individual tests and suggested corrective actions. All glassware is cleaned per SOP NC-QA-014.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.
- 5.2. Eye protection that prevents splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Refer to the TestAmerica North Canton Corporate Environmental Health and Safety Manual for a complete description of personal protection equipment. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated must be removed and discarded; other gloves must be cleaned immediately. Latex, Nitrile and vinyl gloves all provide adequate protection against the methanol used in this method.
- 5.3. 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	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.
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-STEEL	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 degrades the skin. May be absorbed through skin.
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.			

- 5.4. It is recommended that analysts break up work tasks to avoid repetitive motion tasks, such as opening a large number of vials or containers in one time period.
- 5.5. Exposure to chemicals must be maintained as low as reasonably achievable. All samples with stickers that read "Caution/Use Hood!" must be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.
- 5.6. Opened containers of neat standards must be handled in a fume hood.
- 5.7. Sample extracts and standards, which are in a flammable solvent, must be stored in an explosion-proof refrigerator.
- 5.8. When using hydrogen gas as a carrier, all precautions listed in the CSM must be observed.

- 5.9. Standard preparation and dilution must be performed inside an operating fume hood.
- 5.10. 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.
- 5.11. 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.
- 5.12. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. An analytical system complete with a gas chromatograph is required. A data system capable of measuring peak area and/or height is required. Recommended equipment and supplies for individual methods are listed in each method appendix.

7. REAGENTS AND STANDARDS

7.1. Stock Standards

- 7.1.1. Stock standards are purchased as certified solutions or prepared from pure solutions. Stock standards for Method 8021B are stored at -10 to -20°C. Other stock standard solutions are stored as recommended by the manufacturer. All stock standards must be protected from light. Stock standard solutions must be brought to room temperature before using.
- 7.1.2. Semivolatile stock standard solutions must be replaced after one year. Stock standards of gases must be replaced at least every week, unless the acceptability of the standard is demonstrated (Less than 20% drift from the initial calibration is an acceptable demonstration). Other volatile stock standards must be replaced every six months or sooner if comparison with check standards prepared from an independent source indicates a problem.
- 7.1.3. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If vendor-supplied standard has an earlier expiration date then that date is used. Refer to SOP NC-QA-017, Standards and Reagents, for additional information. The standard preparation information is detailed in the Standard Logbook.

7.2. Calibration Standards

7.2.1. Volatile Calibration Standards

- 7.2.1.1. The procedure for preparation of volatile standards is given in Appendix A.

7.2.2. Semivolatile Calibration Standards

- 7.2.2.1. Semivolatile calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method appendices. Semivolatile calibration solutions must be refrigerated at $\leq 6^{\circ}\text{C}$ and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

- 7.3. Gases for carrier and make-up: Hydrogen, Helium, Nitrogen, Zero Air.

7.4. Quality control (QC) Standards

- 7.4.1. QC standards (matrix spiking and Laboratory Control Sample [LCS] standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independent from the calibration standards.

8. SAMPLE PRESERVATION AND STORAGE

- 8.1. The holding time for semivolatile extracts is 40 days from extraction to analysis. Samples must be refrigerated at $\leq 6^{\circ}\text{C}$. Volatile sample storage conditions and holding times are given in Appendix A.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

- 9.1.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.
- 9.1.2. For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2. Batch Definition

- 9.2.1. Batches are defined at the sample preparation stage. Batches must be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the TestAmerica North Canton QC Program document (Policy QA-003) for further details of the batch definition. Ohio VAP projects must reference this SOP instead of policy QA-003 for information on QC.

9.2.2. Quality Control Batch

- 9.2.2.1. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Laboratory generated QC samples (Method Blank, Laboratory Control Sample (LCS), matrix spike / spike duplicate (MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the matrix spike / spike duplicate (MS/MSD) may be replaced with a matrix spike and sample duplicate (MS/SD).

9.3. Control Limits

- 9.3.1. In-house historical control limits may be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined periodically. The recovery limits are mean recovery ± 3 standard deviations, unless that limit is tighter than the calibration criteria, in which case limits may be widened. Project or program specific control limits may be used in place of in-house limits. Refer to Policy QA-003 for more details.
- 9.3.2. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries must be reported unless the dilution is more than 5X.
- 9.3.3. All surrogate, Laboratory Control Sample (LCS), and Matrix Spike (MS) recoveries (except for dilutions) must be entered into LIMS (when available) or other database so that accurate historical

control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes must be reported for all dilutions.

9.3.4. Refer to the QC Program document (Policy QA-003) for further details of control limits.

9.4. Surrogates

9.4.1. All methods must use surrogates to the extent possible. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits. Surrogate recoveries must be met in the method blank (MB) and Laboratory Check Samples (LCS). If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure instrument performance is acceptable.
- Recalculate the data and/or re-analyze the extract if either of the above checks reveals a problem.
- The decision to re-analyze or flag the data must be made in consultation with the client. It is only necessary to reprepare / re-analyze a sample once to demonstrate poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out-of-control results are not due to matrix effect.

Note: For DoD QSM, all surrogates must meet criteria. For Ohio VAP Projects, all surrogates must meet criteria unless the samples are ND and the surrogates are out high. Reanalysis or reparation of the samples is required if these criteria are not met.

9.4.2. If dual column analysis is used, the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.4.3. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate (MS/MSD), then matrix effect has been demonstrated for that sample and reparation is not necessary. If the sample is out of control and the matrix spike (MS) and matrix spike duplicate (MSD) are in control, then reparation or flagging of the data is required. Reparation includes the parent sample and matrix spike / spike duplicate (MS/MSD).

9.4.4. Refer to TestAmerica North Canton QC Program document (Policy QA-003) for further details of the corrective actions.

9.5. Method Blanks

9.5.1. For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous semivolatile samples and sodium sulfate for semivolatile soils tests (Refer to SOPs NC-OP-037, NC-OP-038, NC-OP-039, and NC-OP-040 for details). For low-level volatile soils, the method blank consists of reagent water and Ottawa sand. For medium-level volatile solids, the method blank consists of methanol and Ottawa sand. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the method blank and affected samples will normally be required. Consultation with the client must take place. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted if sufficient volume of sample remains.

- 9.5.2. The method blank must not contain any analyte of interest at, or above, the reporting limit (except common laboratory contaminants, see below) or at, or above, 5% of the measured concentration of that analyte in the associated samples, whichever is higher.
- 9.5.3. If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone, phthalate esters), the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.
- 9.5.4. Re-extraction and re-analysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.
- 9.5.5. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be taken in consultation with the client.

Note: For Ohio VAP projects, the result must be below the reporting limit or samples must be re-extracted unless the samples are non-detect.
- 9.5.6. Refer to TestAmerica North Canton QC Program document (Policy QA-003) for further details of the corrective actions.
- 9.5.7. Refer to SOP NC-QA-016 for further details concerning DoD Project Work.
- 9.6. Laboratory Control Samples (LCS)
 - 9.6.1. For each batch of samples, analyze a Laboratory Control Sample (LCS). The Laboratory Control Sample (LCS) contains a representative subset of the analytes of interest, and must contain the same analytes as the matrix spike. The Laboratory Control Sample (LCS) may also contain the full set of analytes with a subset of control analytes. If any control analyte is outside the laboratory established historical control limits, corrective action must occur. All non-controlling compounds must attain a recovery of 10% or greater if the compound is on the client's list. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted if sufficient volume of sample remains.
 - 9.6.2. If the batch is not re-extracted and re-analyzed, the reasons for accepting the batch must be clearly presented in the project record and the report.
 - 9.6.3. If re-extraction and re-analysis of the batch is not possible due to limited sample volume or other constraints, the Laboratory Control Sample (LCS) is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.
 - 9.6.4. The Laboratory Control Sample (LCS) must have acceptable surrogate recoveries. If surrogate recoveries are low, re-extraction of the Laboratory Control Sample (LCS) and affected samples will normally be required. Consultation with the client should take place. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted if sufficient volume of sample remains.
 - 9.6.5. Refer to TestAmerica North Canton QC Program document (Policy QA-003) for further details of the corrective action.
 - 9.6.6. If dual column analysis is used, the choice of which result to report is made in the same way as for samples (Section 12.1.2), unless one column is out of control, in which case the in control result is reported.
 - 9.6.7. Laboratory Control Sample (LCS) compound lists are included in the appendices.

9.7. Matrix Spikes/Spike Duplicates (MS/MSD)

- 9.7.1. For each QC batch, analyze a matrix spike and matrix spike duplicate (MS/MSD). Spiking compounds and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory-specific historically generated limits.
- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur unless samples for this compound are ND. The initial corrective action must be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the Laboratory Control Sample (LCS) is within limits, then the laboratory operation is in control and analysis may proceed.
 - If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate (MS/MSD) and the Laboratory Control Sample (LCS), the laboratory is out of control and corrective action must be taken. Corrective action must normally include reparation and re-analysis of the batch.
 - If a matrix spike / matrix spike duplicate (MS/MSD) is not possible due to limited sample, then a Laboratory Control Sample (LCS) duplicate may be analyzed if required by client or regulatory programs. The recovery for each spike of the pair must be within established control limits. If the RPD is out of control, but both accuracy recoveries are within acceptance criteria, prepare an NCM and qualify report.
 - The matrix spike / matrix spike duplicate (MS/MSD) must be analyzed at the same dilution as the unspiked sample, unless the matrix spike components would then be above the calibration range.
- 9.7.2. If dual column analysis is used, the choice of which result to report is made in the same way as for samples (Section 12.1.2), unless one column is out of control, in which case the in control result is reported.

9.8. Control Limits

- 9.8.1. Control limits are established by the laboratory as described in SOP NC-QA-018.
- 9.8.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMs.

10. CALIBRATION AND STANDARDIZATION

- 10.1. Internal or external calibration may be used. In either event, prepare standards containing each analyte of interest at a minimum of five concentration levels. The low-level standard must be at, or below, the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in the appendices.
- 10.2. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns, changing PID lamps or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance.
- 10.3. With the exception of Section 10.4 below, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve, AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least five points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points. Third order calibrations require at least seven points.

- 10.4. A level may be removed from the calibration if the reason can be clearly documented (for example, a broken vial or no purge run). A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be re-analyzed and the re-analysis used for the calibration. All initial calibration points in a single calibration curve must be analyzed without any changes to instrument conditions, and all points in a single calibration curve must be analyzed within 24 hours.

10.5. External Standard Calibration

- 10.5.1. Quantitation by the external standard method assumes a proportional relationship between the calibration run and the analyte in the sample. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

$$\text{Calibration Factor or Response Factor (CF) or (RF)} = \frac{\text{Area or Height of Peak}}{\text{Mass Injected (ng)}}$$

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. It is also possible to use the concentration of the standard rather than the mass injected. (This would require changes in the equations used to calculate the sample concentrations). Use of peak area or height must be consistent. However, if matrix interferences would make quantitation using peak area inaccurate for a particular sample, then peak height may be used as a substitute.

10.6. Internal Standard Calibration

- 10.6.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected etc. can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. To use this approach, select one or more internal standard(s) that are similar in analytical behavior to the compounds of interest. Recommended internal standards are given in the appendices. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. If matrix interference is observed, reanalysis of the sample is required. If matrix interference is confirmed, report the second analysis and note in the Case Narrative. . For Ohio VAP projects, the laboratory must re-analyze any sample where the internal standard fails, and there is no evidence of matrix interference. If there is no matrix interference, the sample must be reanalyzed at the original dilution. If the internal standard is within criteria, report the second analysis. If the internal standard is still outside of criteria, the sample must be analyzed at a second dilution. If the internal standard still does not meet criteria, the sample must be diluted until the internal standard meets criteria. Multiple runs may be required.

- 10.6.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows.

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Response for the analyte to be measured

A_{is} = Response for the internal standard

C_{is} = Concentration of internal standard

C_s = Concentration of the analyte to be determined in the standard

10.7. Calibration Curve Fits

10.7.1. Average response factor, linear regression, or quadratic curves may be used to fit the data. Average response factor may be used if the average % RSD of the response factors or calibration factors of all the analytes in the calibration standard taken together is $\leq 20\%$. The average % RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes. NOTE: This is not allowed for Ohio VAP projects or Update IV Methods.

10.7.2. In general, for environmental analysis, average response factors are the most appropriate calibration model. Linear or curved regression fits must only be used if the analyst has reason to believe that the average RF model does not fit the normal concentration/response behavior of the detector. Linear or quadratic curve fits may be used if the compounds have historically exhibited a non-linear response and cannot be used to extend the calibration range for compounds that normally exhibit a linear response, but within a narrower calibration range.

10.7.3. Average Response Factor

The average response factor may be used if the average percent relative standard deviation (% RSD) of all the response factors taken together is $\leq 20\%$.

The equation for average response factor is:

$$\text{Average response factor} = \overline{RF} = \frac{\sum_{i=1}^n RF_i}{n}$$

Where: n = Number of calibration levels

$$\sum_{i=1}^n RF_i = \text{Sum of response factors for each calibration level}$$

10.7.4. Linear Regression

The linear fit uses the following functions:

10.7.4.1. External Standard

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response

x = Concentration

a = Slope

b = Intercept

10.7.4.2. Internal Standard

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b \right]}{a}$$

Where: C_s = Concentration in the sample

A_s = Area of target peak in the sample

A_{is} = Area of internal standard in the sample

C_{is} = Concentration of the internal standard

10.7.5. Quadratic Curve

The quadratic curve uses the following functions:

10.7.5.1. External standard

$$y = ax + cx^2 + b$$

Where c is the curvature

10.7.5.2. Internal Standard

$$y = a \left(\frac{A_s \times C_{is}}{A_{is}} \right) + c \left(\frac{A_s \times C_{is}}{A_{is}} \right)^2 + b$$

10.8. Evaluation of Calibration Curves

10.8.1. The percent relative standard error (% RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.8.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level. The percent relative standard error is calculated as follows.

$$\% RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^N \left[\frac{C_i - PC_i}{C_i} \right]^2}{(N - P)}}$$

Where:

N = Number of points in the curve

P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)

C_i = True concentration for level i

PC_i = Predicted concentration for level i

Note: When average response factors are used, % RSE is equivalent to % RSD.

10.9. The following requirements must be met for any calibration to be used.

- Response must increase with increasing concentration.
- If a curve is used, the calculated intercept of the curve at zero response must be less than \pm the reporting limit for the analyte.
- The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be $\leq 20\%$.
- Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination may be used, and must be greater or equal to 0.990.

Note: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (r) and Coefficient of Determination (r^2) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on r . As a result, a curve may have a very good correlation coefficient (>0.995) while also having $> 100\%$ error at the low point.

10.10. Weighting of Data Points

10.10.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason, it is preferable to increase the weighting of the lower concentration points. $1/\text{Concentration}^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and must be used if the data system has this capability.

10.11. Non-standard analytes are sometimes requested. For these analytes, it may be acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five-point initial calibration. This action must be with client approval. If the analyte is detected in any of the samples, a five-point initial calibration must be generated, and the sample(s) re-analyzed for quantitation.

10.12. Calibration Verification

10.12.1. 12-hour Calibration

10.12.1.1. The working calibration curve or RF must be verified by the analysis of a mid point calibration standard at the beginning, after every 12 hours, and at the end of the analysis sequence.

10.12.2. Daily Calibration Verification

10.12.2.1. It may be appropriate to analyze a mid-point standard more frequently than every 12 hours. If these calibration verification standards are analyzed, requirements are the same as the 12-hour calibration with the exception that retention times are not updated.

10.12.2.2. Any individual compounds with $\% D < 15\%$ meet the calibration criteria. The calibration verification is also acceptable if the average of the $\% D$ for all the analytes is $< 15\%$, or as noted in individual test sections. This average is calculated by summing the entire absolute $\% D$ results in the calibration (including surrogates) and dividing by the number of analytes. Only ND or results below the RL are reported. Any analyte that is reportable as found must have a $\%$ difference of $< 15\%$ in the calibration verification or 12-hour calibration on the column used for quantitation. Refer to Section 12.1.2 for which result to report. Update IV does not allow use of grand mean. CCV must pass by $\pm 20\%$.

- 10.12.3. An ICV is analyzed immediately after an initial calibration. The acceptance criteria is $\pm 20\%$. If this is not met, a new initial calibration curve is analyzed.
- 10.12.4. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.
- 10.12.5. Samples quantitated by external standard methods must be bracketed by calibration verification standards that meet the criteria listed above. The bracketing standards on the column used for calibration must meet the same criteria as the opening standards. Bracketing is not necessary for internal standard methods.
- 10.12.6. If the analyst notes that a CCV has failed and can document the reason for failure (e.g., no purge, broken vial, carryover from the previous sample etc.), then a second CCV may be analyzed without any adjustments to the instrument. If this CCV meets criteria, then the preceding samples have been successfully bracketed. If adjustments to the instrument are performed before the repeat CCV, then the proceeding samples have not been successfully bracketed; but analysis may continue.
- 10.12.7. In general, it is not advisable to analyze repeat CCVs on unattended runs. If repeat CCVs are analyzed, then the first must serve as the bracketing standard for the preceding samples and the last must serve as the CCV for the following samples.
- 10.12.8. If highly contaminated samples are expected, it is acceptable to analyze solvent blanks or primers at any point in the run.
- 10.12.9. Percent Difference Calculation

10.12.9.1. Percent difference for internal and external methods is calculated as follows:

Internal Standard

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

External standard

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where: RF_c and CF_c are the response and calibration factors from the continuing calibration

\overline{RF} and \overline{CF} are the average response & calibration factors from the initial calibration

10.12.10. Percent Drift Calculation

10.12.10.1. Percent drift is used for comparing the continuing calibration to a linear or quadratic curve. The criteria for percent drift are the same as for percent difference

$$\% \text{ Drift} = \frac{\text{Calculated Conc.} - \text{Theoretical Conc.}}{\text{Theoretical Conc.}} \times 100\%$$

10.12.10.2. Corrective Actions for Continuing Calibration

10.12.10.3. If the overall average percent drift of all analytes is greater than $\pm 15\%$, corrective action must be taken. This may include clipping the column, changing the liner, or

other minor instrument adjustments, followed by re-analyzing the standard. If the overall average percent drift still varies by more than $\pm 15\%$, a new calibration curve must be prepared.

10.12.10.4. Corrective Action for Samples

10.12.10.4.1. For internal standard methods, any samples injected after a standard not meeting the calibration criteria must be re-injected.

10.12.10.4.2. For external standard methods, any samples injected after the last good continuing calibration standard must be re-injected.

10.12.10.4.3. If the average percent drift for all the analytes in the calibration is over 15%; but all of the analytes requested for a particular sample have percent drift $\leq 15\%$, then the analysis is acceptable for that sample.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file. Procedural deviations are not allowed for Ohio VAP Projects.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3. Extraction

11.3.1. Extraction procedures are referenced in the SOPs NC-OP-037, NC-OP-038, NC-OP-039, and NC-OP-040, current revision.

11.4. Cleanup

11.4.1. Cleanup procedures are referenced in the SOP NC-OP-025, current revision.

11.5. Gas Chromatography

11.5.1. Chromatographic conditions for individual methods are presented in the appendices.

11.6. Sample Introduction

11.6.1. In general, volatile analytes are introduced using Purge and Trap as described in Appendix A.

11.6.2. Semivolatile analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.7. Analytical Sequence

11.7.1. An analytical sequence starts with an initial calibration or a calibration verification. Refer to the individual method appendices (Appendices A, B, C, D, and E) for method-specific details of calibration verifications and analytical sequences.

11.7.2. The calibration verification includes analysis of standards containing all single response analytes and updating the retention time windows.

- 11.7.3. If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a calibration verification.

11.8. Retention Time Windows

- 11.8.1. Retention time windows must be determined for all analytes. Make an injection of all analytes of interest each day over a three-day period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). For multi-response analytes (e.g., Aroclors), use the retention time of major peaks. Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.
- 11.8.2. The center of the retention time window is the retention time from the last of the three standards. The centers of the windows are updated with the mid-point of the initial calibration and each 12-hour calibration. The widths of the windows must remain the same until new windows are generated following the installation of a new column.
- 11.8.3. If the retention time window as calculated above is less than ± 0.05 minutes, use a retention time window appropriate for the analysis and run time. This allows for slight variations in retention times caused by sample matrix.
- 11.8.4. The laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.
- 11.8.5. Retention time studies are filed in the laboratory.
- 11.8.6. Corrective Action for Retention Times
- 11.8.6.1. The retention times of all compounds in the 12-hour calibration or calibration verification standard must be within the retention time window. If this condition is not met, all samples analyzed after the last compliant standard must be re-analyzed, unless the following conditions are met for any compound that elutes outside the retention time window.
- 11.8.6.2. The retention time of that compound in the standard must be within a retention time range equal to twice the original window.
- 11.8.6.3. No peak that would be reportable must be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.9. Daily Retention Time Windows

- 11.9.1. The center of the retention time windows determined in Section 11.8 is adjusted to the retention time of each analyte as determined in the 12-hour calibration standards or continuing calibration verification standards. (See Methods 8081A and 8082 Appendices B and C for exceptions for multi-response components.) The retention time windows must be updated at the beginning of each analytical sequence and with each 12-hour calibration or continuing calibration verification.

11.10. Procedural Variations

- 11.10.1. Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo and approved by a supervisor and QA/QC Manager. The Nonconformance Memo must be filed in the

project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. Procedural deviations are not allowed for Ohio VAP Projects.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Normally confirmation is required on a second column; but if the detector is sufficiently specific or if the sample matrix is well enough defined, single column analysis may be adequate. In some cases, GC/MS confirmation may be required. Client-specific requirements may also define the need for second column confirmation and/or GC/MS confirmation. Refer to the appendices for test specific requirements for confirmation. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column at a concentration greater than the reporting limit (MDL if J flag confirmation required). Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system. Many programs require chromatograms before and after manual integration. Additional information on manual integration can be found in SOP CA-Q-S-002.

12.1.2. Dual column quantitation

For confirmed results, two approaches are available to the analyst:

- a) the primary column approach, or
- b) the better result approach

Both are acceptable to avoid the reporting of erroneous or unconfirmed data.

12.1.2.1. Primary column approach

12.1.2.2. The result from the primary column is normally reported. The result from the secondary column is reported if any of the following three bulleted possibilities are true.

- There is obvious chromatographic interference on the primary column
- The result on the primary column is 40% greater than the result on the secondary column
- Continuing or bracketing standard fails on the primary column but is acceptable on the secondary column. (If the primary column result is > 40% higher than the secondary and the primary column calibration fails, then the sample must be evaluated for re-analysis.)

12.1.2.3. Better result approach

The higher of the two results is normally reported. The higher result is considered better because the higher result is generally higher because of chromatographic interference. For Ohio VAP projects, the higher result must be reported unless the laboratory can demonstrate that a matrix interference caused the result to be elevated. For Ohio VAP projects both columns must meet calibration criteria. The lower result is reported if any of the following two bulleted possibilities are true.

- There is obvious chromatographic interference on the column with the higher result
- The continuing or bracketing calibration on the column with the higher result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for re-analysis.)

- 12.1.3. If the Relative Percent Difference (RPD) between the response on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

$$RPD = \frac{|R_1 - R_2|}{\frac{1}{2}(R_1 + R_2)}$$

Where: R=Result

12.1.4. Multi-response Analytes

12.1.4.1. For multi-response analytes, the analyst must use the retention time window, but must rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

- 12.1.5. The experience of the analyst must weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2. Calibration Range

- 12.2.1. If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and re-analyzed. Dilutions must target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.3. Dilutions

- 12.3.1. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be re-analyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.3.1.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and only minor matrix peaks are detected, then the sample must be re-analyzed at a more concentrated dilution. Analyst judgement is required to determine the most concentrated dilution that will not result in instrument contamination.

12.3.2. Reporting Dilutions

12.3.2.1. The most concentrated dilution with no target compounds above the calibration range must be reported. Other dilutions may be reported at client request if the lower dilutions will not cause detector saturation, column overload, or carryover. Analyst judgement and client site history will be factors in the reporting of dual dilutions.

12.4. Interferences

- 12.4.1. If peak detection is prevented by interferences, further cleanup must be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5. Internal Standard Criteria

- 12.5.1. If internal standard calibration is used, then the internal standard response in a continuing calibration standard must be within 50 to 150% of the response in the mid level of the initial calibration.
- 12.5.2. The internal standard response in samples must be within 50-150% of the response of previous continuing calibration standard.

12.6. Calculations

- 12.6.1. Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in an appendix attached to this document.

12.6.2. External Standard Calculations

12.6.2.1. Aqueous samples

$$\text{Concentration (mg / L)} = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times V_s)}$$

Where:

A_x = Response for the analyte in the sample

V_i = Volume of extract injected, μL

D_f = Dilution factor

V_t = Volume of total extract, μL

V_s = Volume of sample extracted or purged, mL

CF = Calibration factor, area or height/ng

12.6.2.2. Non-aqueous Samples

$$\text{Concentration (mg / kg)} = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times W)}$$

Where:

W = Weight of sample extracted or purged, g

12.6.2.3. Internal Standard Calculations

12.6.2.4. Aqueous Samples

$$\text{Concentration (mg / L)} = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times V_s)}$$

Where:

C_{is} = Amount of internal standard added, ng

A_{is} = Response of the internal standard

RF = Response factor for analyte

12.6.2.5. Non-aqueous Samples

$$\text{Concentration (mg / kg)} = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times W \times D)}$$

12.6.3. Surrogate Recovery

12.6.3.1. Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equation.

$$\% \text{ Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100$$

12.6.4. Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.1.1. Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in SOPs NC-QA-021 and CA-Q-S-006.

13.2. Initial Demonstration

13.2.1. Each laboratory must make a one-time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests, it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample must be equivalent to a mid-level calibration.

13.2.1.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in each appendix.

13.2.1.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

13.3.1. The Group/Team Leader has the responsibility to ensure an analyst who has been properly trained in its use and has the required experience performs this procedure.

14. POLLUTION PREVENTION

- 14.1. 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".

15. WASTE MANAGEMENT

- 15.1. All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."
- 15.2. Waste Streams Produced by the Method
- 15.2.1. The following waste streams are produced when this method is carried out.
- 15.2.1.1. Vials containing sample extracts. These vials are placed in the vial waste located in the GC/MS laboratory.
- 15.2.1.2. **Tubes containing sample extracts for TPH, pesticides, PCBs, and herbicides.** These capped tubes are placed in the PCB/flammable waste located the GC prep laboratory.
- 15.2.1.3. Samples, standards, and all extraction materials contaminated with high levels (>50ppm) of PCB's must be segregated into their own waste stream. PCB wastes are collected in one of three waste streams, solid PCB, liquid PCB and PCB vial waste. PCB containing samples are located through a LIMS query and disposed of as PCB containing.
- 15.2.1.4. **Extracted solid samples contaminated with methylene chloride/acetone or acetone/hexane.** These materials are disposed of in the solid waste and debris in a red container located in the Extractions Lab.
- 15.2.1.5. **Discarded samples.** These samples are collected in the solid debris drum.

16. REFERENCES

- 16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, and Section 8000B
- 16.2. [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version
- 16.3. TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version
- 16.4. [Corporate Quality Management Plan \(COMP\)](#), current version

16.5 Revision History

Historical File:	Revision 2.1: 08/12/96	Revision 0: 01/21/08 (NC-GC-038)
(formerly CORP-GC-0001NC)	Revision 3.0: 12/01/97	Revision 1: 01/15/09 (NC-GC-038)
	Revision 5.3: 11/18/99	
	Revision 5.4: 11/10/00	
	Revision 5.5: 03/16/01	
	Revision 5.6: 05/25/01	
	Revision 5.7: 10/01/03	
	Revision 5.8: 02/06/06	

16.2. Associated SOPs and Policies, current version

- 16.5.1 QA Policy, [QA-003](#)
- 16.5.2 Glassware Washing, [NC-QA-014](#)
- 16.5.3 Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)
- 16.5.4 Method Detection Limits and Instrument Detection Limits, [NC-QA-021](#) and [CA-Q-S-006](#)
- 16.5.5 Standards and Reagents, [NC-QA-017](#)
- 16.5.6 Cleanup Procedures for Organic Extractable Samples, [NC-OP-025](#)
- 16.5.7 Supplemental Practices for DoD Project Work, [NC-QA-016](#)
- 16.5.8 Acceptable Manual Integration Practices, [CA-Q-S-002](#)
- 16.5.9 Calibration Curves (General), [CA-Q-S-005](#)
- 16.5.10 Section of Calibration Points, [CA-T-P-002](#)
- 16.5.11 Continuous Liquid / Liquid Extraction of Organic Compounds from Waters Based on Methods SW846 3520C and 600 Series and Waste Dilution Based on Method 3580A, [NC-OP-037](#)
- 16.5.12 Separatory Funnel Extraction of Organic Compounds from Waters Based on Methods SW846 3510C and 600 Series and Waste Dilution Based on Method, [NC-OP-038](#)
- 16.5.13 Sonication Extraction of Organic Compounds from Soils Based on Method SW846 3550C and Waste Dilution Based on Method 3580A, [NC-OP-039](#)
- 16.5.14 Soxhlet (Traditional) Extraction of Organic Compounds from Soils Based on Method SW846 3540C and Waste Dilution Based on Method 3580A, [NC-OP-040](#)

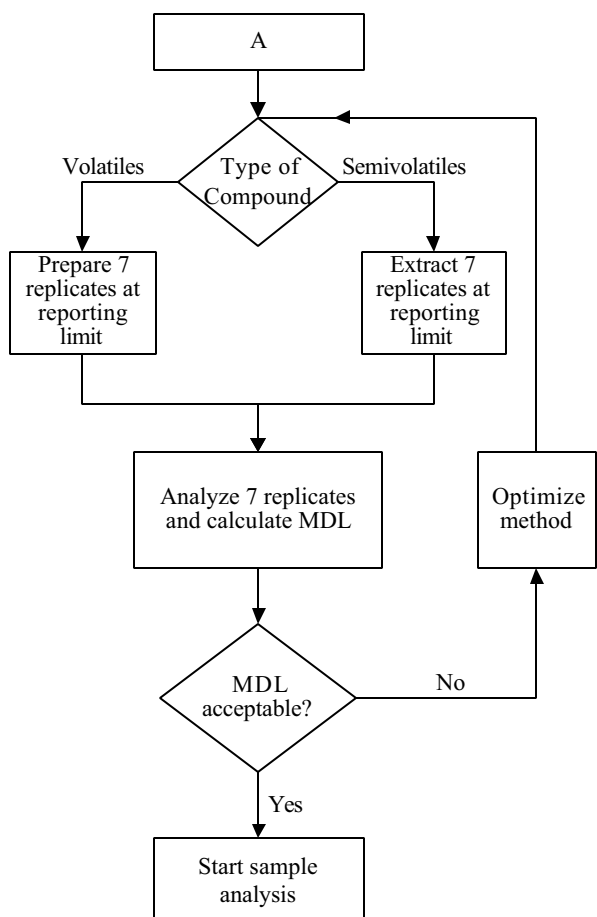
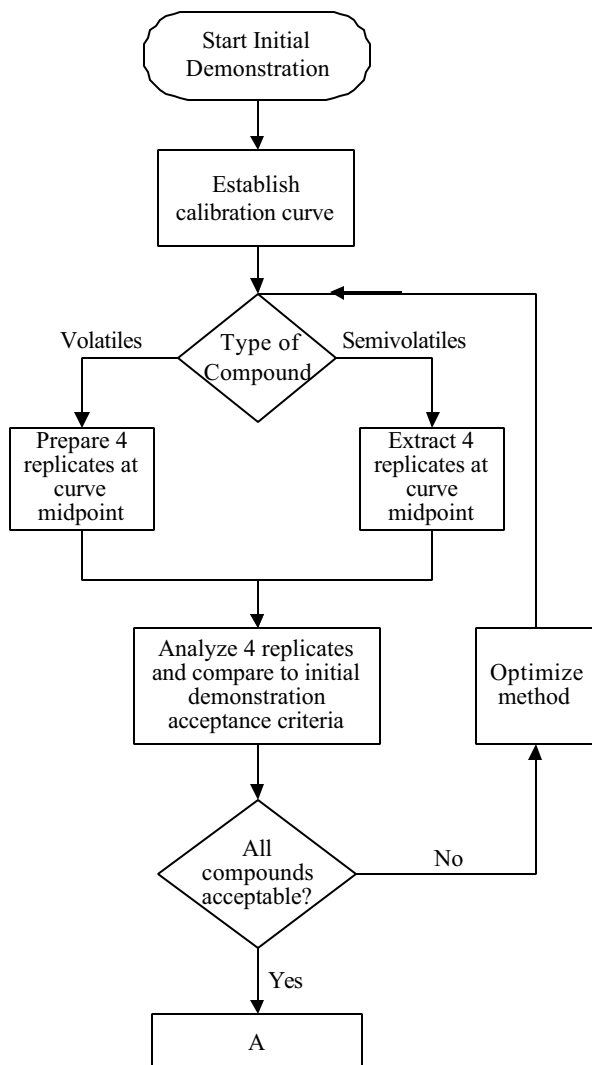
17. MISCELLANEOUS

17.1. Modifications from Reference Method

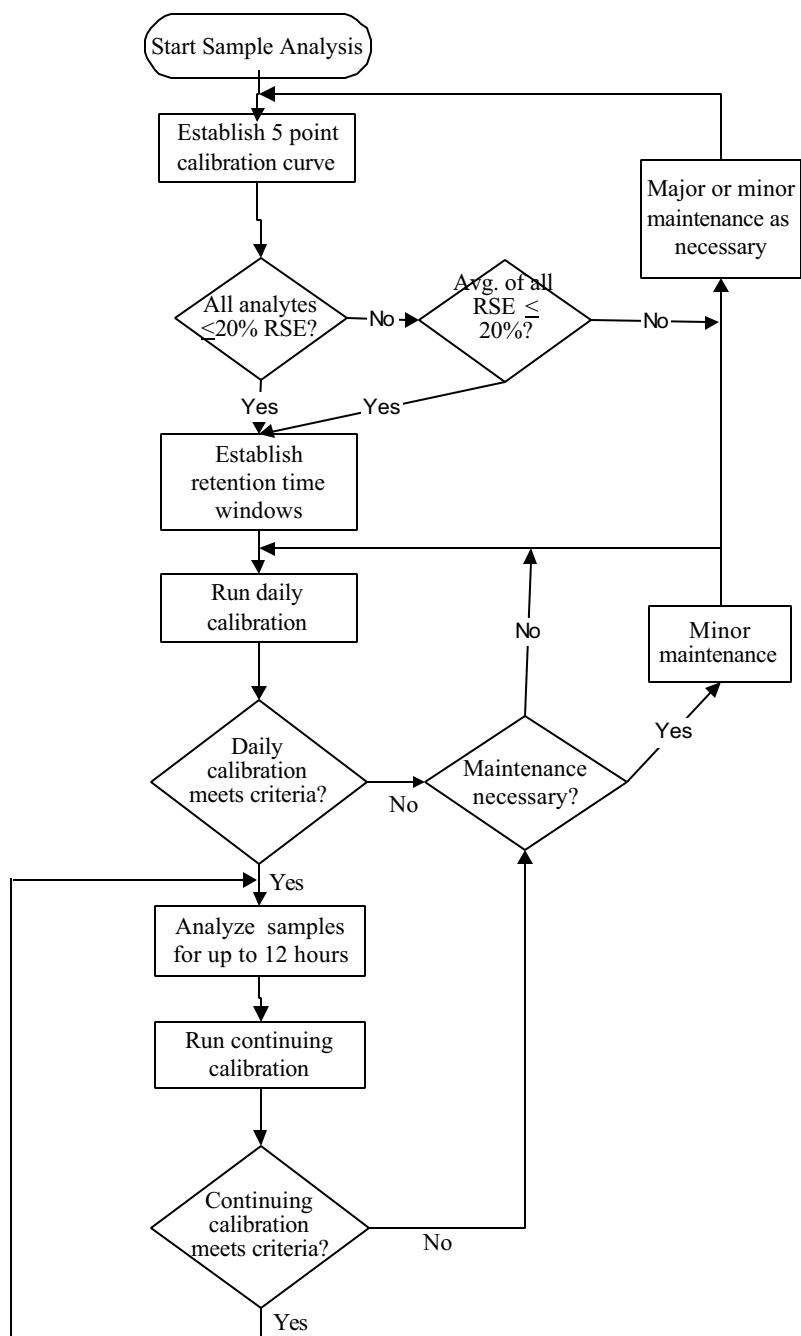
- 17.1.1. Chapter 1 of SW-846 states the method blank must not contain any analyte of interest at, or above, the Method Detection Limit. This SOP states the Method Blank must not contain any analyte of interest at, or above, the reporting limit. Common lab contaminants are allowed to be up to five times the reporting limit in the method blank following consultation with the client.

17.2. Flow Diagrams

17.2.1. Initial demonstration and MDL



17.2.2 Sample Analysis¹



¹ This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

1. SCOPE AND APPLICATION

- 1.1. This SOP Appendix describes sample preparation and extraction for the analysis of volatile organics by a Purge and Trap procedure following Method 8021B. All requirements of the 8000B section of this SOP must be met except when superseded by this Appendix. Refer to Table A1 for the individual analytes normally determined by these procedures. Routine reporting limits are listed in Table A1.
- 1.2. Compounds within the scope of this method have boiling points below 200°C and are insoluble or slightly soluble in water.
- 1.3. Water samples and soils samples with low levels of contamination may be analyzed directly by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in soil may be determined by the medium level methanol extraction procedure.
- 1.4. This method also describes the preparation of water-miscible liquids, non-water-miscible liquids, solids, wastes, and soils/sediments for analysis by the Purge and Trap procedure.

2. SUMMARY OF METHOD

- 2.1. An inert gas is bubbled through the sample at ambient temperature or at 40°C (40°C required for low-level soils), and the volatile components are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and back-flushed with inert gas to desorb the components onto a gas chromatographic column. Analytes are detected using a photo-ionization detector, an electrolytic conductivity detector, or a combination of both.
- 2.2. For soil samples, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water. It is then analyzed by Purge and Trap GC following the normal water method.

3. DEFINITIONS

- 3.1. Refer to the TestAmerica North Canton Quality Assurance Manual (QAM), current version, for definitions of terms and acronyms used in this document.

4. INTERFERENCES

- 4.1. Refer to the main body of this SOP for general information on chromatographic interferences.
- 4.2. Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device must be avoided.
- 4.3. Samples can be contaminated by diffusion of volatile organics through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.
- 4.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it must be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the

system are subject to contamination. Therefore, frequent bake-out and purging of the system may be required.

- 4.5. A holding blank is kept in the sample refrigerator. This is analyzed and replaced every seven days. If the holding blank does not meet the method blank criteria, the source of contamination must be found and corrected. Evaluation of all samples analyzed in the seven-day period prior to the analysis of the contaminated holding blank is required. Refer to SOP NC-QA-020 for additional information on holding blanks.

5. SAFETY

- 5.1. Refer to the main body of this SOP for general safety requirements.
- 5.2. Benzene has been tentatively classified as known or suspected human or mammalian carcinogens.
- 5.3. GC VOA instruments use an ultraviolet (UV) light source, which must be shielded from view.

6. EQUIPMENT AND SUPPLIES

- 6.1. Microsyringes – 5 µL, 10µL, 25µL, 100µL, 250µL, 500µL, and 1000µL. These must be equipped with a 20 gauge (0.006" ID) needle. These must be used to measure and dispense methanolic solutions and aqueous samples.
- 6.2. Purge and Trap Apparatus -- A device capable of extracting volatile compounds, trapping on a sorbent trap, and introducing onto a gas chromatograph.
- 6.3. Purge and Trap Autosampler -- In order to maintain high sample throughput, an autosampler is highly recommended.
- 6.4. Trap -- The trap used is dependent on the class of compound to be analyzed. Refer to Table A2 for suggested traps for specific tests.
- 6.5. Purge Vessels -- These are dependent on the purge and trap unit/autosampler used. Both disposable culture tubes (needle sparge units) and specially designed vessels with fritted bottoms may be used. Follow the manufacturer's suggestions for configuration.
- 6.6. Columns -- Refer to Table A2 for details of columns
- 6.7. Volumetric flasks, Class A -- 5 mL to 250 mL
- 6.8. pH paper: Range 0-14
- 6.9. Balance capable of weighing to 0.01g for samples
- 6.10. Chlorine test strips
- 6.11. Hach chlorine test pillows
- 6.12. Mechanical pipettes: 5 mL, 10 mL and 20 mL

7. REAGENTS AND SUPPLIES

- 7.1. Refer to the main body of this SOP for general requirements for reagents and supplies.

7.2. Organic-Free Water

- 7.2.1. Organic-free water is defined as water in which an interferent is not observed at the reporting limit of the compounds of interest. The laboratory method for generating organic free water is continuously sparging water with helium or nitrogen.

7.3. Methanol -- Purge and Trap Grade

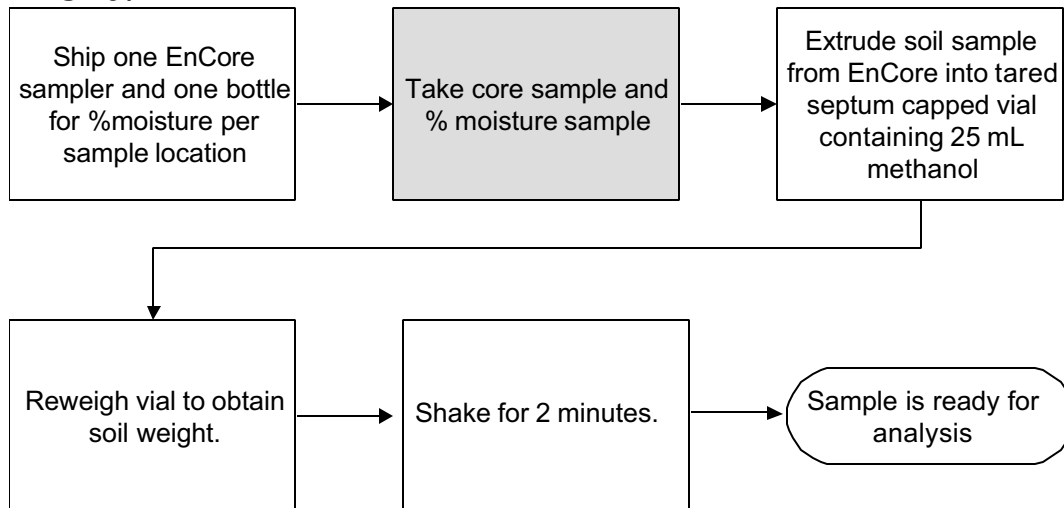
7.4. Standards

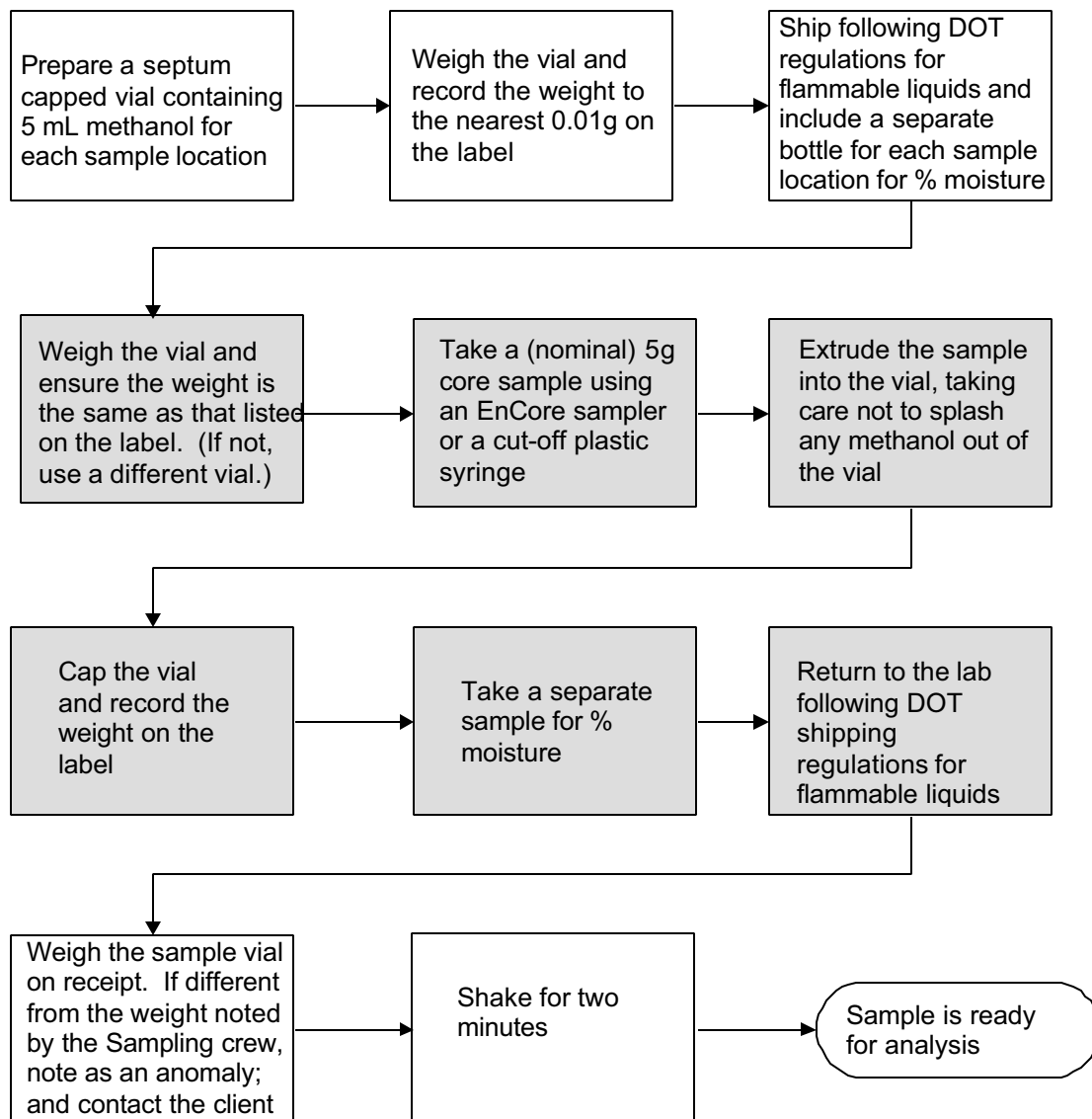
- 7.4.1. Refer to Table A3 for details of surrogate, matrix spiking, and internal standards. Calibration standard levels are not specified, since they may depend on the sensitivity and linear range of specific detectors. However, the low-level standard must be equivalent to the reporting limits specified in Table A1.
- 7.4.2. Volatile standards are prepared by injecting a measured volume of the stock standard into a volumetric flask containing the appropriate volume of methanol. See the Standards Logbook for details on sample preparation.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1. Holding times for all volatile analysis are 14 days from sample collection to analysis.
- 8.2. Water samples are normally preserved at pH < 2 with 1:1 hydrochloric acid. Unpreserved samples must be analyzed within seven days from sample collection.
- 8.3. Solid samples are field preserved with methanol for medium-level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.
- 8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore™ sample. (The 5g or 25g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium-level procedure. If very low detection limits are needed (< 50 µg/kg for most analytes), then it will be necessary to use two additional 5g EnCore™ samplers or to use field preservation.
- 8.5. Sample collection for medium-level analysis using EnCore™ samplers.
- 8.5.1. Ship one 5g (or 25g) EnCore™ sampler per field sample position.
- 8.5.2. An additional bottle must be shipped for percent moisture determination.
- 8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25g sampler). Obtain the weight of the soil added to the vial and note on the label.
- 8.5.4. Add the correct amount of surrogate spiking mixture. (Add 1 µL of a 50 µg/mL solution for a nominal 5g sample, 50 µL for a medium level prep sample, 50 µL for a waste prep, and 2.5 mL for a 25g soil sample.)
- 8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples (MS/MSD). (Add 10 µL of a 10 µg/mL solution for a nominal 5g sample, 500 µL for a medium level prep sample, 500 µL for a waste prep, and 2.5 mL for a 25g soil sample.) The addition of spike introduces a slight error (0.4%), which can be neglected, into the calculations.

- 8.5.6. Prepare a Laboratory Control Sample (LCS) for each batch by adding the correct amount of matrix spiking solution to clean methanol. (Add 10 µL of a 10 µg/mL solution for a nominal 5g sample, 500 µL for a medium level prep sample, 500 µL for a waste prep, and 2.5 mL for a 25g soil sample.)
- 8.5.7. Method blanks are prepared using 5 g of Ottawa sand, 5mL of reagent water, and a stir bar.
- 8.5.8. Shake the samples for two minutes to distribute the methanol throughout the soil.
- 8.5.9. Allow to settle and store in a clean Teflon®-capped vial at $4 \pm 2^{\circ}\text{C}$ until analysis.
- 8.6. Sample collection for medium level analysis using field methanol preservation
 - 8.6.1. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.
 - 8.6.2. Add the correct amount of surrogate spiking mixture. (Add 250 µL of 50 µg/mL solution for a nominal 25 g sample, 50 µL for a nominal 5g sample.)
 - 8.6.3. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 µL of 250 µg/mL solution for a nominal sample.) The addition of spike introduces a slight error (0.4%), which can be neglected, into the calculations.
 - 8.6.4. Prepare a Laboratory Control Sample (LCS) for each batch by adding the correct amount of matrix spiking solution to clean methanol. (500 µL of 10 µg/mL spike to 5 mL methanol or 20 µL spike to 5 mL methanol).
 - 8.6.5. For medium level Method Blanks, prepare 5 mL of methanol, 50µL of surrogate and 5 g of Ottawa sand in a 20 mL vial.
 - 8.6.6. Shake the samples for two minutes to distribute the methanol throughout the soil.
 - 8.6.7. Allow to settle and store in a clean Teflon®-capped vial at $4 \pm 2^{\circ}\text{C}$ until analysis.
- 8.7. Aqueous samples are stored in glass containers with Teflon®-lined septa at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ with minimum headspace. For volatile water samples, the method blank consists of reagent water
- 8.8. Medium-level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon®-lined caps and stored at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The extracts are stored with minimum headspace.
- 8.9. The maximum holding time is 14 days from sampling until the sample is analyzed. Maximum holding time for the EnCore™ sampler (before the sample is added to methanol) is 48 hours.
- 8.10. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise, it is replaced every 14 days.

**EnCore procedure when low level is not required (field steps
in gray)**

Field methanol extraction procedure (field steps in gray)

9. QUALITY CONTROL

- 9.1. Refer to the main body of this SOP for general quality control procedures, including batch definition, requirements for method blanks, Laboratory Control Sample (LCS), matrix spikes/ spike duplicate (MS/MSD), surrogates, and control limits.
- 9.2. Refer to Table A4 for the components and levels of the Laboratory Control Sample (LCS) and matrix spikes / spike duplicates (MS/MSD) mixes.

10. CALIBRATION AND STANDARDIZATION

- 10.1. Refer to the main body of this SOP for general calibration procedures.
- 10.2. Gas Chromatograph Operating Conditions
 - 10.2.1. Various column configurations are possible. If dual column confirmation is necessary, the sample may be split using a Y splitter at the injector end to direct the sample to two columns and two detectors.
 - 10.2.2. Refer to Tables A2, A3, and A4 for GC operating conditions. Additional operating instruction may be found in instrument manuals located in the laboratory.
- 10.3. Initial Calibration
 - 10.3.1. Refer to Section 10 of the Method 8000B section of this SOP for details of initial calibration criteria.
 - 10.3.2. Low-level soil samples must be purged at 40°C; therefore the calibration curve must also be purged at 40°C.
 - 10.3.3. The low-level calibration must be at the reporting limit or below. The remaining standards encompass the working range of the detector. See Table A5 for the I-cal level and amounts.
 - 10.3.4. Calibrate the instrument using the same volume that will be used during sample analysis.
- 10.4. Initial Calibration Verification (ICV)
 - 10.4.1. An initial calibration verification (ICV) standard is analyzed immediately following the initial calibration. Acceptance criteria is $\pm 20\%$. If this is not met, a new initial calibration curve is analyzed.
- 10.5. Daily Calibration Verification
 - 10.5.1. A mid-level calibration standard is used for the calibration verification. Acceptance criteria is $\pm 15\%$.
 - 10.5.2. A calibration verification run is performed after every ten samples or 12 hours for this method.
 - 10.5.3. Bracketing of samples with calibration verification runs is only necessary for external standard analysis. Analytes are detected using a photo-ionization detector are quantitated using the internal standard method.

11. PROCEDURE

- 11.1. Refer to the main body of this SOP for general procedural requirements.

11.2. Analytical Sequence

- 11.2.1. The analytical sequence starts with an initial calibration of at least five points or a 12-hour calibration that meets % difference criteria from an existing initial calibration.

11.3. Confirmation

- 11.3.1. The PID detector is sufficiently selective that second column confirmation is not always necessary. Requirements for second column confirmation must be decided in consultation with the client.

11.4. Aqueous and Soil Sample Analysis (Autosampler Purge and Trap units that sample directly from the VOA vial)

- 11.4.1. Check the pH of the sample in the VOA vial prior to analysis. Samples are also checked for residual chlorine at this time.
- 11.4.2. Units, which sample from the VOA vial, should be equipped with a module, which automatically adds surrogate and internal standard solution, as needed, to the sample prior to purging the sample.
- 11.4.3. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise, the internal and surrogate standards must be added to the vial.
Note: Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to be analyzed as soils.
- 11.4.4. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.5. Low-Level Solids Analysis using discrete autosamplers Bulk Solids

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

- 11.5.1. This procedure cannot be used for Ohio VAP samples. Refer to Section 1.4 for the appropriate procedure.
- 11.5.2. Do not discard any supernatant liquids. Mix the contents of the container
- 11.5.3. *Weigh out 5g (or other appropriate aliquot) of sample into a disposable culture tube or 40mL vial. Record the weight to the nearest 0.1g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 0.5g. If the sample is contaminated with analytes such that a purge amount less than 0.5g is appropriate, use the medium-level method described in Section 8.6, Appendix A.*
- 11.5.4. *Place in autosampler.*
- 11.5.5. *Before placing on the autosample, add 5 mL of organic free water to each vial. Add surrogate/internal standard (and matrix spike solutions if required.) (See Table A3.) Add directly to the sample from Section 11.8.1.*

11.5.6. *The above steps must be performed rapidly and without interruption to avoid loss of volatile organics*

11.6. Methanol Extract Soils

11.6.1. Take an appropriate aliquot from the sample prep container. Add to 5mL of organic free water in a 40 mL VOA vial. Turn off the automatic surrogate function on the autosampler. Place the sample in the autosampler and analyze as for aqueous samples. If less than 1µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume not less than 1µL will be added to the water in the VOA vial.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the main body of this SOP. Refer to Tables A5 and A6 for details of the calibration curves.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced in the Method 8000B section of this SOP.

14. POLLUTION PREVENTION

14.1. Refer to Section 14 of the main body of this SOP

15. WASTE MANAGEMENT

15.1. Refer to Section 15 of the main body of this SOP

15.2. Waste streams produced by the method.

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

15.2.1.1. **Acidic material from the auto-sampler.** Waste stream must be collected and neutralized before discharge to a sewer system if the pH is less than 4.

15.2.1.2. **Methanol waste standards.** Methanol waste is discarded as a flammable liquid.

15.2.1.3. **All samples including purged and extracted soils and waters:** Samples are collected in boxes and removed from the lab to storage. The waste coordinator handles crushing the vials and proper disposal.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Sections 5000, 5030B, 5035 and 8021B.

16.2. SW846, *Test Methods for Evaluating Solid Waste*, Third Edition, Closed System Purge and Trap and Extraction for Volatile Organics in Soil and Waste Samples, Method 5035, Rev 0, December 1996.

16.3. Laboratory Holding Blanks, [NC-QA-020](#)

17. MISCELLANEOUS

17.1. Tables

TABLE A1

Standard Analyte List for Method 8021B				
Compound	CAS No.	Reporting Limit, µg/L or µg/kg		
		Aqueous	Low Soil	Medium Soil
1,2,4-Trimethylbenzene	95-63-6	1.0	1.0	50
1,3,5-Trimethylbenzene	108-67-8	1.0	1.0	50
Benzene	71-43-2	1.0	1.0	50
Ethylbenzene	100-41-4	1.0	1.0	50
Methyl tert-butyl ether (MTBE)	1634-04-4	1.0		
Toluene	108-88-3	1.0	1.0	50
Xylenes (total)	1330-20-7	1.0	1.0	50

TABLE A2

Recommended Conditions for Method Combined Aromatic and Halogenated Volatiles	
Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4°C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	RTX - Volatiles 120m x 0.53mm ID df = 2.0um
Carrier gas	Hydrogen
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

TABLE A3

Surrogate and Internal Standard Concentrations			
Components	Working Solution µg/mL	Spike amount µL	Final concentration µg/L (µg/kg)
Fluorobenzene (IS)	50	1	10
a,a,a-Trifluorotoluene (SS)	50	1	10

TABLE A4

Concentrations for Laboratory Control Sample (LCS) and MS/MSD Compounds			
Components	Working Solution µg/mL	Spike A µL	Final Concentration µg/L (µg/kg)
Benzene	10	10	20
Ethylbenzene	10		20
m&p Xylenes	20		40
o-Xylene	10		20
Xylenes, Total	30		60
MTBE	10		20
1,2,4-Trimethylbenzene	10		20
1,3,5-Trimethylbenzene	10		20
Toluene	10		20

TABLE A5

Initial Calibration for Water Analysis		
Cal Level	On Column Amount (ng)	Final Concentration (ug/L)
1	5	1
2	10	2
3	50	10
4	100	20
5	200	40
6	400	80
7	800	160

TABLE A6

Soil or Water Heated Initial Calibration Curve		
Cal Level	On Column Amount (ng)	Final Concentration (ug/kg)
1	5	1
2	10	2
3	50	10
4	100	20
5	200	40
6	400	80
7	800	160

1. SCOPE AND APPLICATION

- 1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8081A and 8081B is applied to the analysis of organochlorine pesticides by GC/ECD. This appendix applicable to extracts derived from any matrix which are prepared according to the appropriate sample extraction SOPs.
- 1.2. Table B1 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2. SUMMARY OF METHOD

- 2.1. This method presents conditions for the analysis of prepared extracts of organochlorine pesticides. The pesticides are injected onto the column and separated and detected by electron capture detection. Quantitation is by external standard methods.

3. DEFINITIONS

- 3.1. Refer to the TestAmerica North Canton Quality Assurance Manual (QAM), current version, for definitions of terms and acronyms used in this document.

4. INTERFERENCES

- 4.1. Refer to the main body of this SOP for information regarding chromatographic interferences.
- 4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Avoiding contact with any plastic materials minimizes interferences from phthalates.
- 4.3. Sulfur will interfere and can be removed using procedures described in SOP NC-OP-025, Cleanup SOP.
- 4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Using hexane / acetone as the extraction solvent (rather than hexane / methylene chloride) will reduce the amount of interferences extracted.

5. SAFETY

- 5.1. Refer to main body of this SOP for general safety requirements.
- 5.2. The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, and the BHCs. Primary standards of these toxic compounds must be prepared in a hood.
- 5.3. All ⁶³Ni sources must be leak-tested every six months, or in accordance with the manufacturer's general radioactive material license.
- 5.4. All ⁶³Ni sources must be inventoried every six months. If a detector is missing, the Director, EH&S must be immediately notified, and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

- 6.1. A ⁶³Ni electron capture detector is required.

- 6.2. Refer to Table B2 for analytical columns.
- 6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.
- 6.4. Autosampler vials, inserts, and caps

7. REAGENTS AND STANDARDS

- 7.1. Refer to the main body of this SOP for general requirements for reagents and supplies.
- 7.2. Refer to Table B3 for details of calibration standards. See the Standards Logbook for details on sample preparation.
- 7.3. Surrogate Standards
 - 7.3.1. Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Refer to Tables B5 and B6 for details of surrogate standards.
- 7.4. Column Degradation Evaluation Mix
 - 7.4.1. A mid-level standard containing 4,4'-DDT and Endrin and not containing any of their breakdown products must be prepared for evaluation of degradation of these compounds by the GC column and injection port. This solution also contains the surrogates. Refer to Table B4 for details of the column degradation evaluation mix.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. The holding time for pesticide extracts is 40 days from extraction to analysis. Samples must be refrigerated at $\leq 6^{\circ}\text{C}$.

9. QUALITY CONTROL

- 9.1. Refer to the main body of this SOP (Section 9) for general quality control procedures, including batch definition, requirements for method blanks, Laboratory Control Sample (LCS), matrix spike / spike duplicate (MS/MSD), surrogates, and control limits.
- 9.2. Refer to Table B5 for the components and levels of the Laboratory Control Sample (LCS) and matrix spikes / spike duplicates (MS/MSD) mixes.

10. CALIBRATION AND STANDARDIZATION

- 10.1. Refer to the main body of this SOP for general calibration requirements.
- 10.2. Refer to Table B2 for recommended details of GC operating conditions. The conditions listed must result in resolution of all analytes listed in Table B1 on both columns.
- 10.3. Column Degradation Evaluation
 - 10.3.1. Before any calibration runs, either initial or 12 hour, the column evaluation mix must be injected before each initial or daily calibration. The degradation of DDT and endrin must be calculated (see Equations 9 and 10) and each shown to be less than 15% before calibration can proceed. This is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

- 10.3.2. If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:
- 10.3.3. Replacement of the injection port liner or the glass wool.
- 10.3.4. Cutting off a portion of the injection end of a capillary column.
- 10.3.5. Replacing the GC column.
- 10.4. Initial Calibration
 - 10.4.1. Refer to Section 10 of the Method 8000B section of this SOP for details of calibration procedures. The low-level calibration standard must be at, or below, the reporting limit.
 - 10.4.2. Refer to Table B7 for the initial calibration analytical sequence.
 - 10.4.3. The response for each single-peak analyte must be calculated by the procedures described in the main body of this SOP.
 - 10.4.4. The surrogate calibration curve is calculated from the AB mix. If there are resolution problems, then the A and B mixes may be analyzed separately.
 - 10.4.5. For multi-component pesticides:
 - 10.4.5.1. A calibration with a minimum of five points is used for multi-component pesticides (typically toxaphene and technical chlordane). Two options are possible; the same quantitation option must be used for standards and samples. Refer to Section 12.3 for guidance on which option to use.
 - 10.4.5.2. A full calibration for any of the multi-component analytes is analyzed.
- 10.5. Daily 12-hour Calibration Verification
 - 10.5.1. The 12-hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12-hour calibration. A mid-level calibration standard is used for the 12-hour calibration. For Method 8081B, the CCV acceptance criteria is $\pm 20\%$
 - 10.5.2. At a minimum, the 12-hour calibration includes analysis of the breakdown mix followed by mid-level standards of the AB mix. At a minimum, multi-component analytes are analyzed at the beginning of a sequence.
 - 10.5.3. The retention time windows for any analytes included in the 12-hour calibration are updated.
- 10.6. Initial Calibration Verification (ICV)
 - 10.6.1. An initial calibration verification (ICV) standard, from a second source, is analyzed immediately following the initial calibration. Acceptance criteria is $\pm 20\%$. If this is not met, a new initial calibration curve is analyzed.

10.7. Daily Continuing Calibration

- 10.7.1. A mid-level AB calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spike / spike duplicate (ms/msd), Laboratory Control Sample (LCS), and method blanks. If 12 hours elapse, analyze the 12-hour standard sequence instead. The continuing calibration standard need not include multi-component analytes. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

11. PROCEDURE

- 11.1. Refer to the main body of this SOP for general procedural requirements.
- 11.2. Suggested gas chromatographic conditions are given in Table B2.
- 11.3. Allow extracts to warm to ambient temperature before injection.
- 11.4. The suggested analytical sequence is given in Table B7.

12. DATA ANALYSIS AND CALCULATIONS

- 12.1. Refer to the main body of this SOP for identification and quantitation of single component analytes.
- 12.2. Identification of Multi-Component Analytes
- 12.2.1. Retention time windows are also used for identification of multi-component analytes, but the “fingerprint” produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst’s judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.
- 12.3. Quantitation of Multi-Component Analytes
- 12.3.1. Use 3-10 major peaks (or total area for quantitation) as described in Section 10.4.4, initial calibration of multi-component analytes.
- 12.3.2. If there are no interfering peaks within the envelope of the multi-component analyte, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.
- 12.3.2.1. Multiple peak option
- 12.3.3. This option is particularly valuable if toxaphene is identified but interferences make quantitation based on total area difficult. Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per multi-peak pesticide, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e., peaks which are significantly larger than would be expected from the rest of the pattern.)

- 12.3.4. Chlordane may be quantitated either using the multiple peak option (Section 12.3.1, Appendix B), total area option (Section 12.3. 2., Appendix B), or by quantitation of the major components, α -chlordane, γ -chlordane and heptachlor.
- 12.4. Second column confirmation multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence. For Ohio VAP projects, both columns must meet criteria.
- 12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.
- 12.6. Calculation of Column Degradation/% Breakdown (%B)

Equation 9

$$DDT \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100$$

Where:

A_{DDD} , A_{DDE} , and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

Equation 10

$$Endrin \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_E} \times 100$$

Where:

A_{EK} , A_{EA} , and A_E = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

13. METHOD PERFORMANCE

- 13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced in the main body of this SOP.

14. POLLUTION PREVENTION

- 14.1. Refer to Section 14 of the main body of this SOP.

15. WASTE MANAGEMENT

- 15.1. Refer to Section 15 of the main body of this SOP.

16. REFERENCES

- 16.1. SW846, Update III, December 1996, Method 8081A
- 16.2. SW846, Revision 2, February 2007, 8081B

17. MISCELLANEOUS

- 17.1. Modifications from Reference Method - None

17.2. Tables

TABLE B1

Standard Analyte List and Reporting Limits for Methods 8081A and 8081B			
Compound	Reporting Limit, µg/L or µg/kg		
	Water	Soil	Waste
Aldrin	0.05	1.7	50
α-BHC	0.05	1.7	50
β-BHC	0.05	1.7	50
δ-BHC	0.05	1.7	50
γ-BHC (Lindane)	0.05	1.7	50
α-Chlordane	0.05	1.7	50
γ-Chlordane	0.05	1.7	50
Chlordane (technical)	0.5	17	500
4,4'-DDD	0.05	1.7	50
4,4'-DDE	0.05	1.7	50
4,4'-DDT	0.05	1.7	50
Dieldrin	0.05	1.7	50
Endosulfan I	0.05	1.7	50
Endosulfan II	0.05	1.7	50
Endosulfan Sulfate	0.05	1.7	50
Endrin	0.05	1.7	50
Endrin Aldehyde	0.05	1.7	50
Heptachlor	0.05	1.7	50
Heptachlor Epoxide	0.05	1.7	50
Methoxychlor	0.1	3.3	100
Toxaphene	2.0	67	2000
APPENDIX IX ADD-ONS			
Diallate	1.0	33	1000
Isodrin	0.1	3.3	100
Chlorobenzilate	0.25	16.7	500
Kepone ¹	1.0	33	1000
Hexachlorobenzene	0.05	33	1000

¹ Kepone is sometimes requested for analysis by method 8081A. However, kepone may produce peaks with broad tails that elute later than the standard by up to a minute (presumably due to hemi-acetal formation). As a result kepone analysis by 8081A is unreliable and not recommended. Analysis by method 8270C is a possible alternative.

Note: alpha chlordane, gamma chlordane, and endrin ketone are not required for some projects. The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.		Final Vol.
Ground water	1000 mL	5 mL	
Low-level soil	30g		10 mL
High-level soil / waste	1g		10 mL

TABLE B2	
Recommended Conditions for Methods 8081A and 8081B	
Parameter	Recommended Conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	120°C for 1 min, 8.5°C/min to 285°C, , 6 min hold
Column 1	Rtx-CLPesticides 30m x 0.53mm id, 0.5µm
Column 2	Rtx CLPesticideII 30m,0.53mm id, 0.5µm
Injection	1µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

TABLE B3						
Calibration Levels ng/mL for Methods 8081A and 8081B						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6 ²
Individual Mix AB¹						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Methoxychlor	5	10	25	50	100	200
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
β-BHC	5	10	25	50	100	200
δ-BHC	5	10	25	50	100	200
α-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
α-Chlordane ³	5	10	25	50	100	200
γ-Chlordane ³	5	10	25	50	100	200
Multi-component Standards						
Chlordane (Technical)	20	50	100	200	500	
Toxaphene	200	500	1000 ⁵	2000	5000	
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

¹ Standards may be split into an A and B mix if resolution of all compounds on both columns is not obtained.

² Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.

³ Compounds may be used in lieu of running a daily technical Chlordane standard for samples that are non-detect for technical Chlordane.

TABLE B4	
Column Degradation Evaluation Mix ng/mL for Methods 8081A and 8081B	
Component	Concentration
4,4'-DDT	25
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

TABLE B5			
Laboratory Control Sample (LCS)/Matrix Spike/Spike Duplicate (MS/MSD) and Surrogate Spike levels µg/L or µg/kg for Methods 8081A and 8081B			
	Aqueous	Soil	Waste
gamma BHC (Lindane)	1	33.3	1000
Aldrin	1	33.3	1000
Heptachlor	1	33.3	1000
Dieldrin	1	33.3	1000
Endrin	1	33.3	1000
Alpha BHC	1	33.3	1000
Beta BHC	1	33.3	1000
Delta BHC	1	33.3	1000
Gamma BHC	1	33.3	1000
4,4'DDD	1	33.3	1000
4,4'DDE	1	33.3	1000
4,4'DDT	1	33.3	1000
Endosulfan I	1	33.3	1000
Endosulfan II	1	33.3	1000
Endosulfan Sulfate	1	33.3	1000
Heptachlor Epoxide	1	33.3	1000
Methoxychlor	1	33.3	1000
Endrin Ketone	1	33.3	1000
Endrin Aldehyde	1	33.3	1000
Alpha-chlordane	1	33.3	1000
Gamma-chlordane	1	33.3	1000
Tetrachloro-m-xylene (Surrogate)	0.20	6.7	200
Decachlorobiphenyl (Surrogate)	0.20	6.7	200

TABLE B6

Laboratory Control Sample (LCS)/Matrix Spike/Spike Duplicate (MS/MSD) and Surrogate Spike levels for TCLP $\mu\text{g/L}$ or $\mu\text{g/kg}$ for Methods 8081A and 8081B	
	Aqueous
Heptachlor	2
Heptachlor epoxide	2
Lindane	2
Endrin	2
Methoxychlor	4

TABLE B7

Suggested Analytical Sequence for Methods 8081A and 8081B**Initial Calibration**

Solvent blank (optional)
 Primer if needed
 Breakdown Mix
 Individual mix AB All levels
 ICV
 Technical Chlordane Level 3¹
 Toxaphene Level 3¹
 Up to 20 samples unless 12 hours comes first)
 Solvent blank (optional)
 Individual mix AB Mid level (Continuing calibration)
 Samples
 After 12 hours:
 Breakdown mix
 Individual mix AB
 Any other single component analytes
 Any multi-component analytes

¹ A curve with a minimum of five points for any of the multi-component analytes may be included.

Note: A solvent blank or primer may be analyzed at any time during the sequence when highly contaminated samples are expected. A solvent blank or primer may not be analyzed as routine immediately prior to standards.

Note: The initial primer is used if the instrument has been idle for a period of time.

12 -Hour Calibration

At least every 12 hours, counting from the start of the initial calibration or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix AB and a PEM must be analyzed if the analysis is to continue.

1. SCOPE AND APPLICATION

- 1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8082 or 8082A is applied to the analysis of polychlorinated biphenyls (PCB) by GC/ECD. This appendix is applicable to extracts derived from any matrix which are prepared according to the appropriate sample extraction SOPs. PCBs are determined and quantitated as Aroclor mixes.
- 1.2. Tables C1 and C5 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

Note: SW-846 method 8082 and 8082A provides incomplete guidance for determination of individual PCB congeners. This SOP does not include directions for congener specific analysis.

2. SUMMARY OF METHOD

- 2.1. This method presents conditions for the analysis of prepared extracts of PCBs. The PCBs are injected onto the column and separated and detected by electron capture detection. Quantitation is by external standard methods.

3. DEFINITIONS

- 3.1. Refer to the TestAmerica North Canton Quality Assurance Manual (QAM), current version, for definitions of terms and acronyms used in this document.

4. INTERFERENCES

- 4.1. Refer to the main body of this SOP for information regarding chromatographic interferences.
- 4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Avoiding contact with any plastic materials minimizes interferences from phthalates.
- 4.3. Sulfur will interfere and can be removed using procedures described in SOP NC-OP-025.
- 4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts. These cleanup procedures are included in SOP NC-OP-025.

5. SAFETY

- 5.1. Refer to the main body of this SOP for general safety requirements.
- 5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.
- 5.3. All ⁶³Ni sources must be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.
- 5.4. All ⁶³Ni sources must be inventoried every six months. If a detector is missing, the EH&S Director must be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

- 6.1. A ^{63}Ni electron capture detector is required.
- 6.2. Refer to Table C2 for analytical columns.
- 6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.
- 6.4. Autosampler vials, inserts, and caps

7. REAGENTS AND STANDARDS

- 7.1. Refer to the main body of this SOP for general requirements for reagents and supplies.
- 7.2. Refer to Table C3 for details of calibration standards. See the Standards Logbook for details on sample preparation.
- 7.3. Surrogate Standards
 - 7.3.1. Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Refer to Table C4 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. The holding time for PCB extracts is 40 days from extraction to analysis. Samples must be refrigerated at $\leq 6^{\circ}\text{C}$.

9. QUALITY CONTROL

- 9.1. Refer to main body of this SOP for general quality control procedures, including batch definition, requirements for method blanks, Laboratory Control Sample (LCS), matrix spikes / spike duplicate (MS/MSD), surrogates, and control limits.
- 9.2. Refer to Table C4 for the components and levels of the Laboratory Control Sample (LCS) and matrix spikes / spike duplicates (MS/MSD) mixes.

10. CALIBRATION AND STANDARDIZATION

- 10.1. Refer to the main body of this SOP for general calibration requirements.
- 10.2. Update IV recommends analysis of DDT and analogs DDD and DDE prior to calibration to assure there is not interference with major 1254 peaks.
- 10.2. Initial Calibration
 - 10.2.1. Refer to Table C6 for the initial calibration analytical sequence.
 - 10.2.2. The response for each Aroclor must be calculated by the procedures described in the main body of this SOP with the following modifications.
 - 10.2.3. A minimum five-point calibration of all Aroclors is generated. The average response factor is used to quantitate Aroclors. The low-level standard must be at or below the reporting limit. The other standards define the working range of the detector.
 - 10.2.4. The high and low standards for the initial calibration of 1016 / 1260 define the acceptable quantitation range for the other Aroclors. If any Aroclor is determined above this concentration, the extract must be diluted and re-analyzed.

Note: For Ohio VAP, Aroclor 1268 may be analyzed. In order to meet project-specific reporting limits, a lower concentration standard may be added to the calibration curve.

- 10.2.5. If the analyst knows that a specific Aroclor is of interest for a particular project, that Aroclor may be used for the calibration rather than the 1016 / 1260 mix.
- 10.2.6. The surrogate calibration curve is calculated from the Aroclor 1016/1260 mix. Surrogates in the other calibration standards are used only as retention time markers.
- 10.2.7. The following is used for the quantitation of all Aroclors. The same quantitation option must be used for standards and samples.
 - 10.2.7.1. Multiple peak option.
 - 10.2.7.2. Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks.
- 10.3. Daily 12-Hour Continuing Calibration
 - 10.3.1. The 12-hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12-hour calibration. For Method 8082A, the CCV acceptance criteria is $\pm 20\%$.
 - 10.3.2. At a minimum, the 12-hour calibration includes analysis of the Aroclor 1260 / 1016 mix.
 - 10.3.3. Other Aroclors are included in the daily calibration check.
 - 10.3.4. The retention time windows for any analytes included in the daily calibration and CCVs are updated.
 - 10.3.5. For this method, samples must be bracketed with successful calibration verification runs.
- 10.4. Initial Calibration Verification (ICV)
 - 10.4.1. An initial calibration verification (ICV) standard, from a second source, is analyzed immediately following the initial calibration. Acceptance criteria is $\pm 20\%$. If this is not met, a new initial calibration curve is analyzed.
- 10.5. Daily Calibration Verification Standards
 - 10.5.1. The Aroclor 1260/1016 calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples, including matrix spikes, Laboratory Control Sample (LCS), and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.)
 - 10.5.2. A mid-level standard is used for the calibration verification.

11. PROCEDURE

- 11.1. Refer to the main body of this SOP for general procedural requirements.
- 11.2. Suggested gas chromatographic conditions are given in Table C2.

11.3. Allow extracts to warm to ambient temperature before injection.

11.4. The suggested analytical sequence is given in Table C6.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification of Aroclors

12.1.1. Retention time windows are used for identification of Aroclors, but the “fingerprint” produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst’s judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.1.2. A clearly identifiable Aroclor pattern serves as confirmation of single column GC analysis.

12.2. Quantitation of Aroclors

12.2.1. Use 3-10 major peaks or total area for quantitation

12.2.2. If the analyst believes that a combination of Aroclor 1254 and 1260 or a combination of 1242, 1248 and 1232 is present, then only the predominant Aroclor is quantitated and reported; but the suspicion of multiple Aroclors is discussed in the narrative. If well-separated Aroclor patterns are present, then multiple Aroclors may be quantitated and reported.

12.3. Second column confirmation of Aroclors will only be performed when requested by the client or regulatory program. The appearance of the multiple peaks in the sample usually serves as a confirmation of Aroclor presence. For Ohio VAP projects, both columns must meet criteria.

12.4. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX). Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits, or if one is <10%.

Note: For Ohio VAP samples and DoD projects, all surrogates must meet acceptance limits, unless the surrogate is biased high and the sample is ND.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced in the main body of this SOP.

13.2. Method detection limits (MDL) are determined for all Aroclors.

14. POLLUTION PREVENTION

14.1. Refer to Section 14 of main body of this SOP.

15. WASTE MANAGEMENT

15.1. Refer to Section 15 of the main body of this SOP

16. REFERENCES

16.1. SW846, Update III, December 1996, Method 8082

16.2. SW846, Update IV, Revision 1, February 2007, Method 8082A

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Method 8082 and 8082A includes limited direction for congener specific quantitation. This is outside the scope of this SOP.

17.2. Tables

TABLE C1			
Standard Analyte list and Reporting Limits for Methods 8082 and 8082A			
	Reporting Limit, µg/L or µg/kg		
Compound	Water	Soil	Waste
Aroclor-1016	1.0	33	1000
Aroclor-1221	1.0	33	1000
Aroclor-1232	1.0	33	1000
Aroclor 1242	1.0	33	1000
Aroclor-1248	1.0	33	1000
Aroclor-1254	1.0	33	1000
Aroclor-1260	1.0	33	1000

The following concentration factors are assumed in calculating the Reporting Limits:

	<u>Extraction Vol.</u>	<u>Final Vol.</u>
Ground water	1000 mL	5 mL
Low-level Soil	30g	10 mL
High-level soil / waste	1g	10 mL

TABLE C2	
Instrumental Conditions for Methods 8082 and 8082A	
Parameter	Recommended Conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	DB-5 or Rtx-5 30m x 0.32mm id, 0.5µm, or CLPesticide I, 30m, 0.53mm id, 0.5µm
Column 2	DB 1701 or Rtx 1701 30m x 0.32 mm id, 0.25µm, or CLPesticide II, 30m, 0.53 mm id, 0.5µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	1µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

TABLE C3						
Calibration Levels ug/mL for Methods 8082 and 8082A						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6¹
Aroclor 1016/1260	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1242	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1221 +1254	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1232	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1248	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1262	0.05	0.1	0.2	0.5	1.0	2.0
Aroclor 1268	0.05	0.1	0.2	0.5	1.0	2.0
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	0.0025	0.005	0.01	0.025	0.05	0.1
Decachlorobiphenyl	0.0025	0.005	0.01	0.025	0.05	0.1

¹ Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.

TABLE C4			
Laboratory Control Sample (LCS) / Matrix Spike/Spike Duplicate (MS/MSD) and Surrogate Spike levels for Aroclor analysis µg/L or µg/kg for Methods 8082 and 8082A			
	Aqueous	Soil	Waste
Aroclor 1016/1260	10	333	10,000
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

TABLE C5			
Michigan Analyte List and Reporting Limits¹ for Methods 8082 and 8082A			
Compound	Reporting Limit		
	water (µg/L)	soil (µg/Kg)	
Aroclor-1016	0.2	330	
Aroclor-1221	0.2	330	
Aroclor-1232	0.4	330	
Aroclor 1242	0.2	330	
Aroclor-1248	0.2	330	
Aroclor-1254	0.2	330	
Aroclor-1260	0.2	330	

¹ Reporting Limits are only for samples performed under the Michigan program.

Table C6**Suggested Analytical Sequence for Methods 8082 and 8082A****Initial Calibration**

Injection

1	Solvent blank (optional)	
2	Aroclor 1016/1260	Level 1
3	Aroclor 1016/1260	Level 2
4	Aroclor 1016/1260	Level 3
5	Aroclor 1016/1260	Level 4
6	Aroclor 1016/1260	Level 5
7	Aroclor 1232	An Initial Calibration includes Levels 1-5. A midpoint is used as CCV.
8	Aroclor 1242	An Initial Calibration includes Levels 1-5. A midpoint is used as CCV.
9	Aroclor 1248	An Initial Calibration includes Levels 1-5. A midpoint is used as CCV.
10	Aroclor 1221/1254	An Initial Calibration includes Levels 1-5. A midpoint is used as CCV.
11	Aroclor 1268 or 1262	An Initial Calibration includes Levels 1-5. A midpoint is used as CCV.
12	ICV	
13-32	Sample 1-20 (or as many samples as can be analyzed in 12 hours)	
33	Aroclor 1016/1260	Level 3

Note: A solvent blank or primer may be analyzed at any time during the sequence when highly contaminated samples are expected. A solvent blank or primer may not be analyzed as routine immediately prior to standards.

12-hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Aroclor 1260 / 1016 mix. Mid-level standards of any other Aroclors expected to be present in the samples are also injected.

1. SCOPE AND APPLICATION

- 1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8151A or EPA Method 615 is applied to the analysis of chlorinated phenoxy acid herbicides in extracts prepared by SOP NC-OP-031.
- 1.2. Table D1 lists compounds, which are routinely analyzed by this method and give the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2. SUMMARY OF METHOD

- 2.1. This method presents conditions for the analysis of prepared extracts of phenoxy acid herbicides by gas chromatography. The herbicides, as their methyl esters, are injected onto the column, separated, and detected by electron capture detectors. Quantitation is by external standard methods.

3. DEFINITIONS

- 3.1. Refer to the TestAmerica North Canton Quality Assurance Manual (QAM), current version, for definitions of terms and acronyms used in this document.

4. INTERFERENCES

- 4.1. Refer to the main body of this SOP for general information regarding chromatographic interferences.
- 4.2. Chlorinated acids and phenols cause the most direct interference with this method.
- 4.3. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples.

5. SAFETY

- 5.1. Refer to the main body of this SOP for general safety requirements.
- 5.2. All ⁶³Ni sources must be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.
- 5.3. All ⁶³Ni sources must be inventoried every six months. If a detector is missing, the EH&S Director must be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

- 6.1. A Ni₆₃ electron capture detector is required.
- 6.2. Refer to Table D2 for analytical columns.
- 6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.
- 6.4. Autosampler vials, inserts, and caps

7. REAGENTS AND STANDARDS

- 7.1. Refer to the main body of this SOP for general information on reagents and standards.
- 7.2. Refer to Table D4 for details of calibration standards. See the Standards Logbook for details on sample preparation.
- 7.3. Surrogate Standards
 - 7.3.1. DCAA is the surrogate standard. Refer to Table D4 for details of surrogate standards.

8. SAMPLE PREPARATION, PRESERVATION, AND STORAGE

- 8.1. The holding time for herbicide extracts is 40 days from extraction to analysis. Samples must be refrigerated at $\leq 6^{\circ}\text{C}$.

9. QUALITY CONTROL

- 9.1. Refer to the main body of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes / spike duplicates (MS/MSD).
- 9.2. Refer to Table D3 for the components and levels of the Laboratory Control Sample (LCS) and matrix spikes / spike duplicates (MS/MSD) mixes.

10. CALIBRATION AND STANDARDIZATION

- 10.1. Refer to the main body of this SOP for general calibration requirements.
- 10.2. Refer to Table D2 for recommended instrument operating conditions.
- 10.3. Calibration standards are prepared from purchased standards in the methyl ester form.
- 10.4. The low-level standard must be at or below the laboratory reporting limit.
- 10.5. The response for each analyte must be calculated by the procedures described in the main body of this SOP
- 10.6. Initial Calibration Verification (ICV)
 - 10.6.1. An initial calibration verification (ICV) standard, from a second source, is analyzed immediately following the initial calibration. Acceptance criteria is $\pm 20\%$. If this is not met, a new initial calibration curve is analyzed.
- 10.7. For method 615, the Ical and the CCV must both pass by 10%.
- 10.8. Daily Continuing Calibration
 - 10.8.1. A mid-level calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spike / spike duplicate (ms/msd), Laboratory Control Sample (LCS), and method blanks. If 12 hours elapse, analyze the 12-hour standard sequence instead. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

11. PROCEDURE

11.1. Refer to the main body of this SOP for procedural requirements.

11.2. Extraction

11.2.1. The extraction procedure is described in SOP NC-OP-032.

11.3. Analytical Sequence

11.3.1. The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.3.2. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence.

11.3.3. The daily calibration consists of mid level standards of all analytes of interest. Retention time windows must be updated with the daily calibration.

11.3.4. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the main body of this SOP for identification and quantitation of single component analytes.

12.2. The herbicides are analyzed as their methyl esters, but reported as the free acid. For this reason, it is necessary to correct the results for the molecular weight of the ester versus the free acid. This is achieved through the concentrations of the calibration standards. For example the 20µg/L calibration standard for 2,4-D contains 21.3 µg/L of the methyl ester. No further correction is necessary.

12.3. A routine 10X dilution occurs on final extracts for all samples. Due to a LIMS limitation, the dilution factor field in LIMS cannot be used when a dilution is routine, because the dilution factor is automatically applied to all reference values creating reporting problems. For the herbicide analysis, the extract volume will be 10mL and an aliquot at 10X dilution will be analyzed. The final extract volume recorded on the laboratory bench sheet will be recorded as 100mL to avoid using the dilution factor field in LIMS.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced in the main body of this SOP.

14. POLLUTION PREVENTION

14.1. Refer to Section 14 of the main body of this SOP.

15. WASTE MANAGEMENT

15.1. Refer to Section 15 of the main body of this SOP.

16. REFERENCES

16.1. Method 8151A, SW-846, Update III, December 1996

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. None

17.2. TABLES

TABLE D1				
Standard Analyte List for Method 8151A				
Compound	CAS Number	Reporting Limit, µg/L or µg/kg		
		Aqueous	Soil	Waste
2,4-D	94-75-7	4	80	4000
2,4-DB	94-82-6	4	80	4000
2,4,5-TP (Silvex)	93-72-1	1	20	1000
2,4,5-T	93-76-5	1	20	1000
Dalapon	75-99-0	2	40	2000
Dicamba	1918-00-9	2	40	2000
Dichloroprop	120-36-5	4	80	4000
Dinoseb	88-85-7	0.6	12	600
MCPA	94-74-6	400	8000	400,000
MCP	93-65-2	400	8000	400,000

The following concentration factors are assumed in calculating the Reporting Limits:

	<u>Extraction Vol.</u>	<u>Final Vol.</u>	<u>Dilution Factor</u>
Ground water	1000 mL	10 mL	10
Low-level Soil without GPC	50g	10 mL	10
High-level soil / waste	1g	10 mL	10

Specific reporting limits are highly matrix dependent. The reporting limits listed above are provided for guidance only and may not always be achievable. For special projects, the extracts may be analyzed without any dilution, resulting in reporting limits 20 times lower than those in Table D1.

TABLE D2	
Instrumental Conditions for Method 8151A	
PARAMETER	Recommended conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	80,2/30/170,0/1/180,1
Column 1	CLPesticideI, 30m, 0.53 mm id, 0.5 µm
Column 2	CLPesticide II, 30m, 0.53 mm id, 0.5µm
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Recommended conditions must result in resolution of all analytes listed in Table D1.

The reporting limits listed in Table D1 will be achieved with these calibration levels and a 20-fold dilution of the sample extract. Lower reporting limits can be achieved with lesser dilutions of the sample extract.

TABLE D3			
Laboratory Control Sample (LCS)/Matrix Spike/Spike Duplicate (MS/MSD) and Surrogate Spike levels µg/L or µg/kg ¹ for Method 8151A			
	Aqueous	Soil	Waste
2,4-D	40	400	20000
Silvex	10	100	5000
2,4,5-T	10	100	5000
2,4-DB	40	400	20000
Dalapon	20	200	10000
DCAA (surrogate)	40	400	20000
Dicamba	20	200	10000
MCP	4000	40000	200000
MCPA	4000	40000	200000
Dichloroprop	40	400	2000
Pentachlorophenol	5	50	2500
Dinoseb	6	60	300

¹ Laboratory Control Sample (LCS), MS and SS spikes are as the free acid.

Note: Dinoseb is a poor performing analyte. No corrective action will be taken if recovery is outside acceptance limits.

TABLE D4						
Calibration Levels for Methods 8151A and 615 (ng amount)						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
2,4 D	0.02	0.04	0.08	0.16	0.32	0.64
2,4 DB	0.02	0.04	0.08	0.16	0.32	0.64
2,4,5 T	0.005	0.01	0.02	0.04	0.08	0.16
2,4,5 TP (Silvex)	0.005	0.01	0.02	0.04	0.08	0.16
Dalapon	0.01	0.02	0.04	0.08	0.16	0.32
DCAA (surr)	0.02	0.04	0.08	0.16	0.32	0.64
Dicamba	0.01	0.02	0.04	0.08	0.16	0.32
Dichloroprop	0.02	0.04	0.08	0.16	0.32	0.64
Dinoseb	0.003	0.006	0.012	0.024	0.048	0.096
MCPA	2	4	8	16	32	64
MCP	2	4	8	16	32	64
Pentachlorophenol	0.0005	0.005	0.01	0.02	0.04	0.08

Bold levels indicate CCV

1. SCOPE AND APPLICATION

- 1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8015B or 8015C is applied to the determination of the concentration and **tentative** identification of extractable petroleum (diesel range) hydrocarbon mixes in waters, wastewaters, soils, and sludges. This Appendix is applicable to extracts derived from any matrix which are prepared according to the appropriate sample extraction SOPs.
- 1.2. Table E2 lists compounds, which are routinely determined by this method, and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed. Other analytes may be analyzed by this method if the quality control criteria in Section 9 and the initial demonstration of method performance in Section 13 are met. Reporting limits are also listed in Table E2. The laboratory carbon range for Ohio VAP and BUSTR projects is Middle Distillates (C10-C20) and Heavy Distillates (C20-C34).

2. SUMMARY OF METHOD

- 2.1 This method presents conditions for the analysis of total petroleum hydrocarbons by gas chromatography. The total petroleum hydrocarbon samples are injected into the column, separated, and detected by flame ionization detectors (FID). Quantitation is by external standard methods.

3. DEFINITIONS

- 3.1. Refer to the TestAmerica North Canton Quality Assurance Manual (QAM), current version, for definitions of terms and acronyms used in this document.

4. INTERFERENCES

- 4.1. Refer to the main body of this SOP for general information regarding chromatographic interferences.
- 4.2. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples.

5. SAFETY

- 5.1. Refer to the main body of this SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

- 6.1. A flame ionization detector (FID) is required.
- 6.2. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.
- 6.3. Autosampler vials, inserts, and caps

7. REAGENTS AND STANDARDS

- 7.1. Refer to the main body of this SOP.
- 7.2. The petroleum hydrocarbons (Diesel Fuel) are purchased from a chemical supplier when available. When no chemical supplier is available, the fuels are purchased from public sources. See the Standards Logbook for details on sample preparation.
- 7.3. Refer to Table E3 for details of calibration standards.

7.4. Surrogate Standards

7.4.1. Nonane (C9) is the surrogate standard.

8. SAMPLE PREPARATION, PRESERVATION, AND STORAGE

8.1. The holding time for semivolatile extracts is 40 days from extraction to analysis. Samples must be refrigerated at <6°C.

9. QUALITY CONTROL

9.1. Refer to the main body of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes / spike duplicates (MS/MSD).

9.2. Matrix spikes / spike duplicates (MS/MSD) recoveries are calculated from a diesel calibration.

9.3. Surrogates

9.3.1. Because of the nature of the TPH analysis, - certain petroleum mixtures can override the C9 (Nonane) surrogate.

Note: Ohio VAP rules require reanalysis when surrogate recoveries are outside of control limits. Re-extraction is required if surrogates are outside of control limits.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to the main body of this SOP for general calibration requirements. The low-level calibration standard must be at, or below, the reporting limit.

10.2. Refer to Table E1 for recommended instrument conditions.

10.3. Initial Calibration

10.3.1. Prior to the initial calibration, a marker solution consisting of alkanes from C10-C44 is analyzed, If additional carbon ranges are needed, a separate solution with alkanes from C10-C50 can be analyzed with a modified instrument program. The marker solution establishes the retention time window.

10.3.2. Analyze a diesel calibration calibration, using a minimum of five points, referring to the recommended instrument conditions. The calibration concentrations are 100, 200, 500, 1000, and 2000 ng/uL. A 5000ng/uL standard may be analyzed if needed. The retention time window of C10-C32 must be used for the Diesel calibration. The low-level standard must be at or below the reporting limit. The other standards define the working range of the detector.

Note: For special projects, retention time windows can be customized to reflect additional carbon ranges. The additional carbon ranges are quantitated against the diesel calibration.

10.4. Initial Calibration Verification (ICV)

10.4.1. An initial calibration verification (ICV) standard, from a second source, is analyzed immediately following the initial calibration. Acceptance criteria is $\pm 20\%$. If this is not met, a new initial calibration curve is analyzed.

10.5. Daily Continuing Calibration

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- 10.5.1. Refer to Section 10 of the Method 8000B section of this SOP for general calibration requirements.
- 10.5.2. A mid-range standard of diesel, C10-20, and C20-34 is used, as appropriate, for the CCV. The acceptance criteria is $\pm 15\%$. This marker solution must be analyzed at the beginning of each sequence. For Method 8015C, the CCV acceptance criteria is $\pm 20\%$

11. PROCEDURE

- 11.1. Refer to the main body of this SOP for procedural requirements.
- 11.2. A suggested analytical sequence is given in Table E4.
- 11.3. Petroleum Hydrocarbon Identification and/or Fingerprinting
 - 11.3.1. To identify the type of petroleum hydrocarbon, compare the chromatographic peak pattern to the patterns of known petroleum hydrocarbons analyzed under identical chromatographic conditions. Samples are quantified against diesel, but fingerprinting may be done when client requested.
 - 11.3.2. Positive matching may not be possible, even using site-specific hydrocarbons. Degradation of the pattern can occur during environmental exposure of the fuel. See Table E2 for possible fingerprints.
 - 11.3.3. Samples are quantified against the initial calibration of diesel or DRO on a single column.
 - 11.3.4. The total height or area of the hydrocarbon is determined in the same manner used for the hydrocarbon standard.
 - 11.3.5. If the amount of sample injected into the GC exceeds the working range of the calibration curve, an appropriate dilution is performed before reanalysis.

12. DATA ANALYSIS AND CALCULATIONS

- 12.1. Refer to the main body of this SOP for identification and quantitation of single component analytes.
- 12.2. Surrogate recovery results are calculated and reported for Nonane (C-9). The surrogate must be within QC criteria. Corrective action is only necessary if Nonane (C-9) is outside of acceptance limits, unless the surrogate is high and the sample is ND.

13. METHOD PERFORMANCE

- 13.1. Performance limits for the four replicate initial demonstration of capability are required as referenced in the main body of this SOP.

14. POLLUTION PREVENTION

- 14.1. Refer to Section 14 of the main body of this SOP.

15. WASTE MANAGEMENT

- 15.1. Refer to Section 15 of the main body of this SOP.

16. REFERENCES

- 16.1. SW846, Method 8015B, Nonhalogenated Organics Using GC/FID, Test Methods for Evaluating Solid Waste, Third Edition, USEPA

- 16.2. SW846, Method 8015C, Nonhalogenated Organics by Gas Chromatography, Test Methods for Evaluating Solid Waste, Revision 3, February 2007.

TABLE E1
Recommended Instrument Conditions for Methods 8015B and 8015C

Parameter	Recommended Conditions
Column	RTX-5
Initial Temperature	40°C
Initial Hold Time	4 minutes
Temperature Program	10°C/minute
Final Temperature	280°C
Final Hold Time	10 minutes
Injection	1µL
Carrier Gas	Hydrogen carrier gas - flow rate 5 - 6 mL/min
Detector Gas Mixture	Air hydrogen mixture in a 10:1 ratio, air 80 - 120 mL/min, hydrogen 8 -12 mL/min

TABLE E2
Reporting Limits for TPH Analysis

Analyte	Reporting Limits		
	Water (µg/L)	Solids (mg/kg)	Waste Dilution (mg/kg)
TPH (as Diesel) or DRO	500	16.7	200
C10-C20 (OVAP & BUSTR -Middle Distillates)	500	16.7	
C20-C34 (OVAP & BUSTR – Heavy Distillates)	500	16.7	
Fingerprint Compounds ¹			
Mineral Spirits	Kerosene	Motor Oil	
Hydraulic Oil	Jet Fuel	Stoddard Solvent	

¹ This list represents most of the common petroleum hydrocarbons. The list may be expanded to include other petroleum hydrocarbons.

TABLE E3					
Calibration Levels for Methods 8015B and 8015C (ng/L)					
	Level 1	Level 2	Level 3	Level 4	Level 5
TPH (as Diesel)	100	200	500	1000	2000

TABLE E4**Suggested Analytical Sequence for Method 8015B and 8015C****Initial Calibration**

Solvent blank (optional)	
Primer if needed	
Marker Solution	
Diesel Standard	All levels
ICV	
Up to 20 samples unless 12 hours comes first)	
Mid level Diesel Standard (Continuing calibration)	

Note: A solvent blank or primer may be analyzed at any time during the sequence when highly contaminated samples are expected. A solvent blank or primer may not be analyzed as routine immediately prior to standards.

Note: The initial primer is used if the instrument has been idle for a period of time.

**Title: DETERMINATION OF VOLATILE ORGANICS BY GC/MS BASED
ON METHODS 8260C, 8260B, AND 8260A**

Ohio EPA has not yet reviewed this revision for use under the Ohio VAP program

[Method: EPA Methods 8260C, 8260B, and 8260A]

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1.0 SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Volatile Organic Compounds in waters, wastewater, soils, sludges, and other solid matrices.
- 1.2. This SOP is applicable to Methods 8260B and 8260C. It may also be used for analysis following Method 8260A.
- 1.3. This method can be used to quantify most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, for more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency.
- 1.4. The method is based upon a purge and trap, gas chromatograph/mass spectrometric (GC/MS) procedure. The approximate working range is 5 to 200 µg/L for 5 mL waters, 1 to 40 µg/L for low-level waters, 5 to 200 µg/kg for low-level soils, and 250 to 10,000 µg/kg for medium-level soils. Reporting limits are listed in Tables 1 and 3.
- 1.5. Method performance is monitored through the use of surrogate compounds, matrix spike/matrix spike duplicates, and laboratory control spike samples.

2.0 SUMMARY OF METHOD

- 2.1. Volatile compounds are introduced into the gas chromatograph by the purge and trap method. The components are separated via the chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information.
- 2.2. Aqueous samples are purged directly. Soils are preserved by extracting the volatile analytes into methanol. Soil samples may also be preserved with sodium bisulfate or by freezing and purging directly.
- 2.3. In the purge and trap process, an inert gas is bubbled through the solution at ambient temperature or at 40°C (40°C required for low-level soils) and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbant column where the volatile components are trapped. After purging is completed, the sorbant column (trap) is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is then heated to elute the components, which are detected with a mass spectrometer.
- 2.4. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing the resultant mass spectra and GC retention times. Each identified

component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3.0 DEFINITIONS

- 3.1 Refer to the TestAmerica North Canton Quality Assurance Manual (QAM), current version, for definitions of terms used in this document.

4. INTERFERENCES

- 4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014. The use of ultra high purity gases, prepurged purified reagent water, and approved lots of purge and trap grade methanol will greatly reduce introduction of contaminants. In extreme cases, the purging vessels may be pre-purged to isolate the instrument from laboratory air contaminated by solvents used in other parts of the laboratory.
- 4.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) into the sample through the septum seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination. Refer to SOP NC-QA-020 for additional information on holding blanks.
- 4.3. Matrix interferences may be caused by non-target contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source depending upon the nature and diversity of the site being sampled.
- 4.4. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially on an autosampler. Whenever an unusually concentrated sample is analyzed, it must be followed by one or more blanks to check for cross-contamination. The purge and trap system may require extensive bake-out and cleaning after a high-level sample.
- 4.5. Some samples may foam when purged due to surfactants present in the sample. When this kind of sample is encountered, the sample must be diluted.

5. SAFETY

- 5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately. Cut-resistant gloves **MUST** be worn when opening VOA vials and when doing any other task that presents a strong possibility of getting cut.

5.3. Primary Materials Used

5.3.1. 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
Sodium bisulfate	Irritant	None	Causes mild to severe irritation to the eyes. Prolonged exposure may cause burn if not flushed with water. May cause mild irritation to skin. Prolonged exposure may cause burn if not flushed with water.
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.
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.			

5.4. It is recommended that analysts break up work tasks to avoid repetitive motion tasks, such as opening a large number of vials or containers in one time period.

- 5.5. Exposure to chemicals must be maintained **as low as reasonably achievable**. All samples with a sticker that reads "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made. MS VOA samples may be prepared outside of the hood, unless it is known that concentrations are high.
- 5.6. The preparation of standards and reagents must be conducted in a fume hood with the sash closed as far as the operations will permit. MS VOA standards may be prepared outside of the hood due to low concentrations of analytes.
- 5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and the laboratory Group Leader.
- 5.8. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices outlined in the TestAmerica Corporate Environmental Health and Safety Manual. These employees must have training on the hazardous waste disposal practices initially upon assignment of these tasks, followed by annual refresher training.
- 5.9. Specific Safety Concerns or Requirements
 - 5.9.1. 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.
 - 5.9.2. The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.
 - 5.9.3. 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.
 - 5.9.4. Sodium bisulfate creates Sulfuric Acid when mixed with water.

6. EQUIPMENT AND SUPPLIES

- 6.1. Microsyringes: 10 μ L and larger
- 6.2. Syringe: 5, 25, or 50 mL glass with luerlok tip, if applicable to the purging device.

- 6.3. Balance: Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.01 g
- 6.4. Glassware
 - 6.4.1. Vials: 20 and 40 mL with screw caps and Teflon® liners.
 - 6.4.2. Volumetric flasks: 10 mL, 100 mL, and 500 mL class A with ground-glass stoppers.
- 6.5. Spatula: Wood splints, small and large.
- 6.6. Disposable pipettes: Pasteur, 5 ¾ in.
- 6.7. Pipetters: Drummond, 30 uL to 100 uL, and 10 uL to 25 uL
- 6.8. Waste Dilution Pipette: 1 mL capacity
- 6.9. Methanol Dispensers: 5 mL, 10 mL, and 50 mL
- 6.10. pH paper: Wide range, pH 0-14.
 - 6.10.1 Chlorine Test Paper: 10 ppm to 200 ppm
- 6.11. Gases
 - 6.11.1. Helium: Ultra high purity, gr. 5, 99.999%.
 - 6.11.2. Nitrogen: Ultra high purity from cylinders or gas generators may be used as an alternative to helium for purge gas.
- 6.12. Purge and Trap Device. The purge and trap device consists of the sample purger, trap, and desorber.
 - 6.12.1. Sample Purger. The recommended purging chamber is designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. Alternative sample purge devices may be used provided equivalent performance is demonstrated. Low-level soils are purged directly from a VOA vial.
 - 6.12.2 Trap. A variety of traps may be used, depending on the target analytes required. One of the traps used is the Vocabarb 3000 trap. Other traps such as the OI 10 may be used if the Quality Control criteria are met. Refer also to instrument operating manuals

located within the laboratory.

6.12.3 Desorber. The desorber must be capable of rapidly heating the trap to at least 180°C. Many such devices are commercially available.

6.12.4. Sample Heater. A heater capable of maintaining the purge device at 40°C is necessary for low-level soil analysis.

6.13 Gas Chromatograph/Mass Spectrometer System

6.13.1 Gas Chromatograph. The gas chromatograph (GC) system must be capable of temperature programming.

6.13.2 Gas Chromatographic Columns. Capillary columns are used. Some typical columns are listed below:

6.13.2.1 Column 1. 20m x 0.18 ID DB-624 with 1 µm film thickness.

6.13.2.2 Mass Spectrometer. The mass spectrometer must be capable of scanning 35-300 AMU every two seconds or less, using 70 volts electron energy in the electron impact mode and capable of producing a mass spectrum that meets the required criteria when 50 ng of 4-Bromofluorobenzene (BFB) are injected onto the gas chromatograph column inlet.

6.13.3. GC/MS Interface. In general, direct introduction to the mass spectrometer is used but any interface that achieves all acceptance criteria may be used.

6.13.4. 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. 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 the specified time or scan-number limits. Also, for the non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The NIST/EPA mass spectral library must be used as the reference library. The computer system must also be capable of backing up data for long-term off-line storage.

7. REAGENTS AND STANDARDS

7.1. Reagents

- 7.1.1. Methanol. Purge and Trap grade, high purity
- 7.1.2. Reagent Water. High purity water that meets the requirements for a method blank when analyzed (see Section 9.4). Reagent water may be purchased as commercial distilled water and prepared by purging with an inert gas overnight.
- 7.1.3. Hydrochloric Acid – (1:1 v/v). Reagent grade or equivalent
- 7.1.4. Sodium bisulfate. Reagent grade or equivalent
- 7.2. Standards
 - 7.2.1. Calibration Standard
 - 7.2.1.1. Stock Solutions. Stock solutions may be purchased as certified solutions from commercial sources or prepared from pure standard materials as appropriate. These standards are prepared in methanol and stored in Teflon®-sealed screw-cap bottles with minimal headspace at -10° to -20°C. Note that standard/spiking concentrations or vendors are subject to change.
 - 7.2.1.2. Working standards. A working solution containing the compounds of interest is prepared from the stock solution(s) in methanol on a weekly basis. These standards are stored in the freezer or as recommended by the manufacturer. Working standards are monitored daily by comparison to the initial calibration curve at the beginning of each 12 hour tune sequence. If any of the calibration check compounds drift in the continuing calibration standard response from the initial calibration by more than 20% then corrective action is necessary. This may include steps such as instrument maintenance, preparing a new calibration verification standard or tuning the instrument. If the corrective actions do not correct the problem, then a new initial calibration must be performed.
 - 7.2.1.3. Aqueous Calibration Standards are prepared in reagent water using the secondary dilution standards. These aqueous standards must be prepared daily.
 - 7.2.1.4. If stock or secondary dilution standards are purchased in sealed ampoules, they may be used up to the manufacturer's expiration date.
 - 7.2.1.5. Additional information can be found in SOP NC-QA-017.
 - 7.2.2. Internal Standards. Internal standards are added to all samples, standards, and blank

analyses. Refer to Table 5 for internal standard components.

- 7.2.3. Surrogate Standards. Refer to Table 6 for surrogate standard components and spiking levels.
- 7.2.4. Laboratory Control Sample Spiking Solutions. Refer to Table 7 for LCS components and spiking levels.
- 7.2.5. Matrix Spiking Solutions. The matrix spike contains the same components as the LCS. Refer to Table 7.
- 7.2.6. Tuning Standard. A standard is made up that will deliver 50 ng on column upon injection. A recommended concentration of 50 ng/ μ L of 4-Bromofluorobenzene in methanol is prepared as described in Sections 7.2.1.1 and 7.2.1.2.
- 7.2.7. All standard preparation information is detailed in the LIMS standards and reagents module.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1. Holding times for all volatile analysis are 14 days from sample collection to analysis.
- 8.2. For DoD samples, water samples are normally preserved at $\text{pH} \leq 2$ with 1:1 hydrochloric acid. Unpreserved water samples must be analyzed within seven days of sampling.
- 8.3. Solid samples are field preserved with sodium bisulfate solution or by freezing upon receipt at the laboratory for low-level analysis, or with methanol for medium-level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. Analysis must be completed 14 days from sampling. At specific client request, unpreserved soil samples may be accepted.
- 8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take an EnCore™ sample. Following shipment back to the lab, the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed ($< 50 \mu\text{g/kg}$ for most analytes), then it will be necessary to use two additional 5g EnCore™ samplers or to use field preservation.
- 8.5. Sample collection for medium level analysis using EnCore™ samplers
 - 8.5.1. Ship one 5g EnCore™ sampler per field sample position.
 - 8.5.2. An additional 2 oz plastic bottle must be shipped for percent moisture determination.

- 8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g sample into a tared VOA vial containing 5 mL methanol. Obtain the weight of the soil added to the vial and note on the label.
- 8.5.4. Add the correct amount of surrogate spiking mixture. 5 μ L for a nominal 5g sample.) Refer to Section 17.2 for Michigan project criteria.
- 8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 μ L of 25 μ g/mL solution for a nominal 5 g sample). Reduce the volume of methanol added to ensure the final volume is 5 mL methanol for a nominal 5g sample. Refer to Section 17.2 for Michigan project criteria.
- 8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 μ L spike to 5 mL methanol). Refer to Section 17.2 for Michigan project criteria.
- 8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.
- 8.6. Sample collection for medium-level analysis using field methanol preservation
 - 8.6.1. Prepare a container by adding 5 mL methanol to a IVOA vial).
 - 8.6.2. Seal the bottle and attach a label.
 - 8.6.3. Weigh the bottle to the nearest 0.01g, and note the weight on the label.
 - 8.6.4. Ship with appropriate sampling instructions.
 - 8.6.5. Each sample will require an additional 2 oz plastic bottle with no preservative for percent moisture determination.
 - 8.6.6. At client request, the methanol addition and weighing may also be performed in the field.
 - 8.6.7. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.
 - 8.6.8. Add the correct amount of surrogate spiking mixture. (Add 5 μ L of 2500 ug/mL solution for a nominal 5g sample.) Refer to Section 17.2 for Michigan project criteria.
 - 8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 μ L of 25 μ g/mL solution for a nominal 5g sample.)

Reduce the volume of methanol added to ensure the final volume is 5 mL methanol for a nominal 5g sample. Refer to Section 17.2 for Michigan project criteria.

8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL of spike to 5 mL methanol . Refer to Section 17.2 for Michigan project criteria.

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.7. Low-level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg), low-level soil preservation must be used. However, it is also necessary to take a sample for the medium-level (field methanol preserved or using the EnCore™ sampler) procedure in case the concentration of analytes in the soil is above the calibration range of the low-level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3. The soil sample is taken using a 5g EnCore™ sampling device and returned to the lab. It is recommended that two EnCore™ samplers be used for each field sample position to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials for sodium bisulfate preservation by adding a magnetic stir bar, approximately 1g of sodium bisulfate, and 5 mL of reagent water. Prepare vials for preservation by freezing by adding a stir bar and 5 mL reagent water.

8.7.5. Seal and label the vial. It is strongly recommended that the vial is labeled with an indelible marker rather than a paper label, since paper labels may cause the autosampler to bind and malfunction. The label absolutely must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.01g, and note the weight on the label.

8.7.7. Extrude the soil sample from the EnCore™ sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil..

Note: Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at <-10°C within 48 hours. The sample must be analyzed within 14 days after sampling and stored at a 45 degree angle in the freezer.

8.7.8. Alternatively the sodium bisulfate preservation may be performed in the field. This is not recommended because of the many problems that can occur in the field setting. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional 2 oz plastic bottle with no preservative for percent moisture determination, and an additional VOA vial preserved with methanol for the medium level procedure. Depending on the type of soil, it may also be necessary to ship vials with no or extra preservative.

8.8. *Unpreserved Soils*

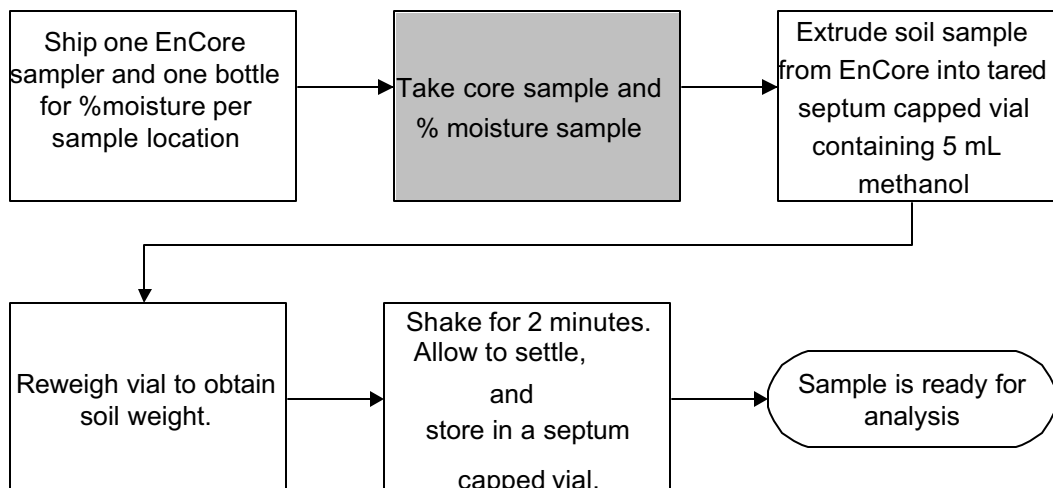
8.8.1. *At specific client request, unpreserved soils packed into glass jars or brass tubes may be accepted and sub-sampled in the lab. This is the old procedure based on Method 5030A and Method 8260A. It is no longer included in SW846 and is likely to generate results that are biased low, possibly by more than an order of magnitude.*

8.9. Aqueous samples are stored in glass containers with Teflon®-lined septa at 4°C ± 2°C with minimum headspace.

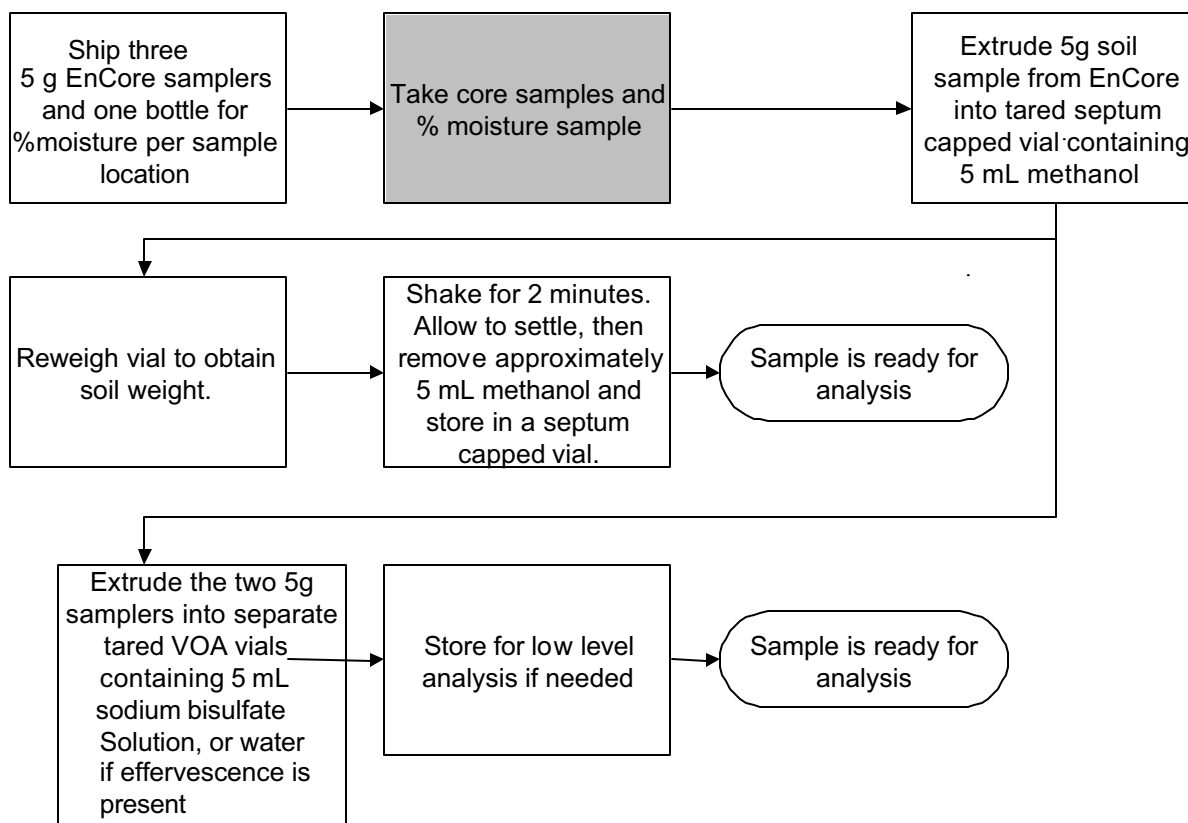
8.10. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14-day holding time. However, they should be analyzed as soon as possible. The lack of preservation must be addressed in the case narrative). Maximum holding time for the EnCore™ sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.11. A holding blank is stored with the samples. This is analyzed weekly. It is replaced every seven days.

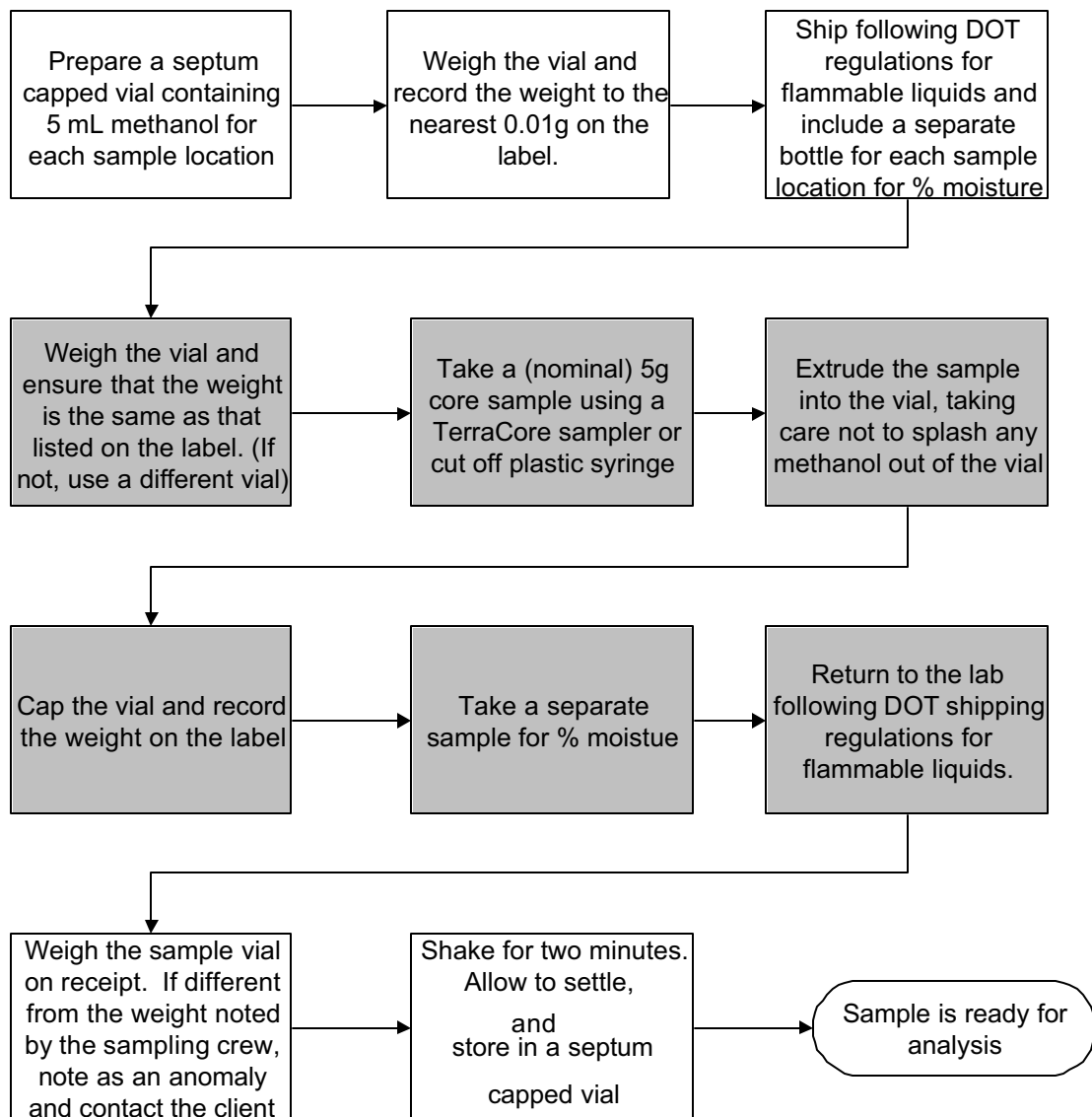
EnCore procedure when low level is not required (field steps in gray)



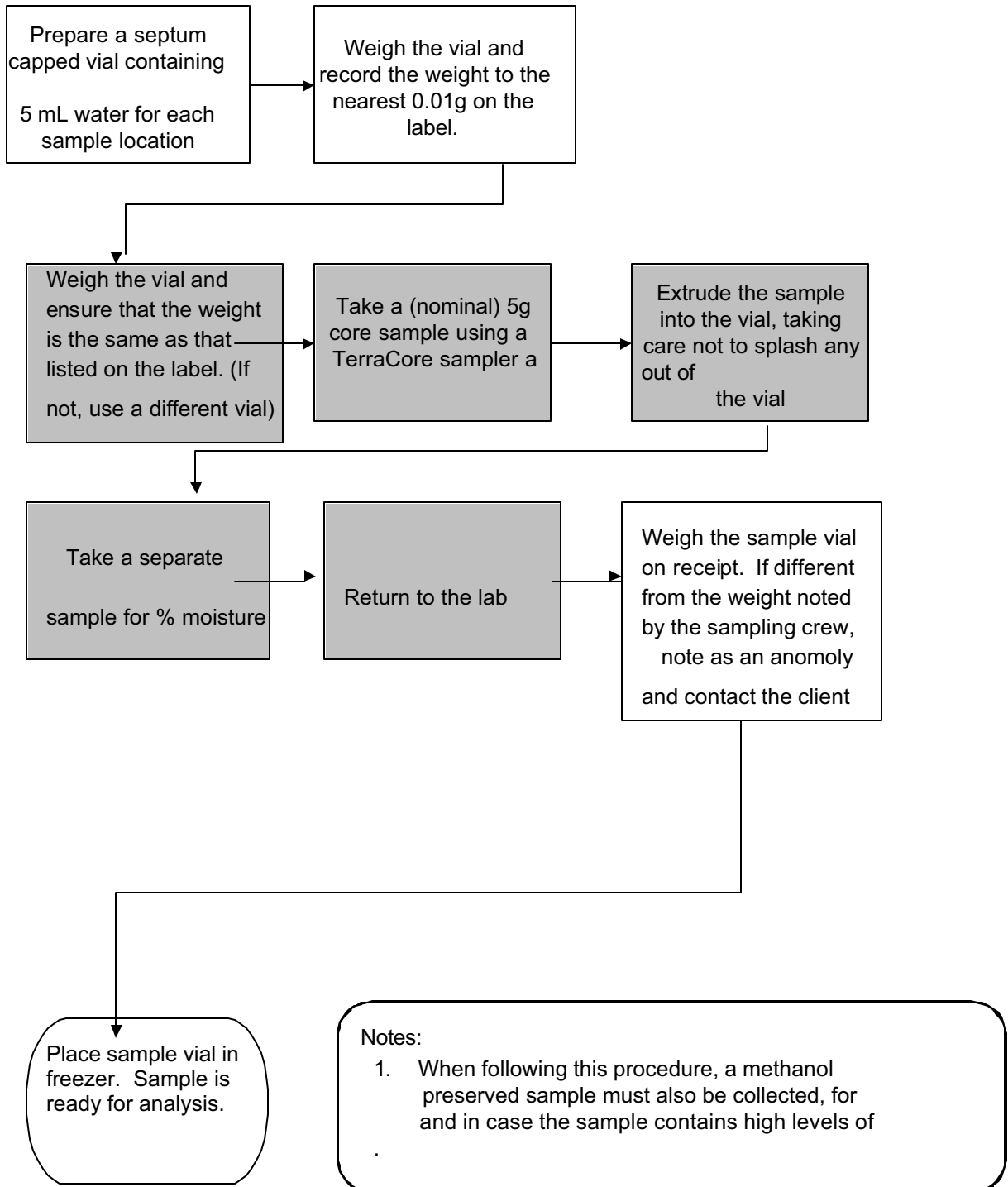
EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



Field water/frozen preservation procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Batch

9.1.1. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. Using this method, each BFB analysis will start a new batch. Batches for medium level soils are defined at the sample preparation stage and may be analyzed on multiple instruments over multiple days, although reasonable effort must be made to keep the samples together.

9.1.1.1. The Quality Control batch must contain a matrix spike/spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Refer to the TestAmerica QC program document (QA-003) for further details of the batch definition.

9.2. Control Limits

9.2.1. Control limits are established by the laboratory as described in SOP NC-QA-018.

9.2.2. Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMs .

9.3. Surrogates

9.3.1. Every sample, blank, and QC sample is spiked with surrogates. Surrogate recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. The compounds included in the surrogate spiking solutions are listed in Table 6. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure instrument performance is acceptable.
- Recalculate the data and/or re-analyze if either of the above checks reveal a problem.
- Reprepate and re-analyze the sample if there is sufficient volume. If there is insufficient volume, the surrogate is narrated.

It is only necessary to reprepare/re-analyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out-of-control results are not due to matrix effect.

9.3.2 If the surrogates are out of control for the sample, matrix spike, and matrix spike

duplicate, then matrix effect has been demonstrated for that sample and re-preparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then re-analysis or flagging of the data is required. For Ohio VAP samples, all surrogates must be in control, or samples must be re-prepared and re-analyzed.

Note: For Ohio VAP and DoD samples, all surrogates must be within acceptance criteria. The exceptions for Ohio VAP are as follows:

(a) insufficient sample for re-extraction, or (b) the surrogates are biased high and the samples are non-detect.

9.3.3 For concrete matrix, Dibromofluoromethane may have poor recovery in samples and matrix spikes. If the surrogate does not meet criteria, no further action is required due to matrix.

9.3.4 Refer to the TestAmerica QC Program document (QA-003) for further details of the corrective actions.

9.4 Method Blanks

9.4.1 For each batch of samples, analyze a method blank. The method blank is analyzed after the calibration standards, normally before any samples. For low-level volatiles, the method blank consists of reagent water. For medium-level volatiles, the method blank consists of the same volume of methanol that was used to prepare the samples. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below). The method blank is acceptable if any compound detected in the blank is present in the associated samples at ten times the blank level. For Ohio VAP work, there can be no target analyte greater than the RL in the method blank unless the sample result is ND. All samples associated with an unacceptable blank will be re-prepared and re-analyzed.

- If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone. Chloroform is a common laboratory contaminant for SPLP.), the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.
- Re-analysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.
- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers.

9.4.2 The method blank must have acceptable surrogate recoveries. If surrogate recoveries

are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client must take place. For Ohio VAP samples, all surrogates must be in control, or reparation of the batch is required.

9.4.3 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

9.4.4 Refer to the TestAmerica QC Program document, Policy QA-003, for further details of the corrective actions.

9.4.5 Refer to SOP NC-QA-016 for further details concerning DoD Project Work.

9.5 Laboratory Control Samples (LCS)

9.5.1 For each batch of samples, analyze an LCS. The LCS is analyzed after the calibration standard, and normally before any samples. The LCS contains a representative subset of the analytes of interest (see Table 7), and must contain the same analytes as the matrix spike. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be reparation and re-analysis of the batch. For Ohio VAP samples, all surrogates must be in control on the LCS, or reparation and re-analysis of the batch is required. The exceptions are as follows: (a) insufficient sample for reparation, (b) expired holding times, or (c) the LCS is biased high and the samples are non-detect for those analytes.

- If the batch is not re-extracted and re-analyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.
- If re-extraction and re-analysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5.2 Refer to the TestAmerica QC Program document (Policy QA-003) for further details of the corrective action.

9.5.3 If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be

expected statistically. These requirements must be negotiated with the client. n-Hexane must be spiked and reported for the LCS for Ohio VAP samples.

- 9.5.4 If full analyte spike lists are used at the client request, it is possible some compounds in the LCS may interfere with each other. In that case, the lab will quantitate those compounds in the LCS with a secondary ion which is free from interferences.

9.6 Matrix Spikes

- 9.6.1 For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in Table 7. Compare the percent recovery and relative percent difference (RPD) to that in the laboratory-specific, historically-generated limits.

- 9.6.2 If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- 9.6.2.1 If the recovery for any component is outside QC limits for both the matrix spike/ spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include re-analysis of the batch.

- 9.6.2.2 The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7 Nonconformance and Corrective Action

- 9.7.1 Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Summary

- 10.1.1. Prior to the analysis of samples and blanks, each GC/MS system must be tuned and calibrated. Hardware tuning is checked through the analysis of the 4-Bromofluorobenzene (BFB) to establish that a given GC/MS system meets the standard mass spectral abundance criteria. The GC/MS system must be calibrated initially at a

minimum of five concentrations (analyzed under the same BFB tune), to determine the linearity of the response utilizing target calibration standards. Once the system has been calibrated, the calibration must be verified each twelve hour time period for each GC/MS system.

10.1.2. General

Electron Energy:	70 volts (nominal)
Mass Range:	35–300 AMU
Scan Time:	To give at least 5 scans/peak, but not to exceed 2 seconds/scan
Injector Temperature:	200–250°C
Source Temperature:	According to manufacturer's specifications
Transfer Line	Temperature: 250–300°C
Purge Flow:	40 mL/minute
Carrier Gas	Flow: 0.4 – 0.6 mL/minute

10.2 Gas chromatograph suggested temperature program

10.2.1 BFB Analysis

Initial Temperature:	100°C
Initial Hold Time:	0.1 minute
Temperature Program:	20°C/minute
Final Temperature:	200°C

10.2.2 Sample Analysis

Initial Temperature:	40°C
Initial Hold Time:	2minutes
Temperature Program:	15°C/minute
Final Temperature:	200°C
Final Hold Time:	3 minutes

10.3. Instrument Tuning

10.3.1. Each GC/MS system must be hardware-tuned to meet the abundance criteria listed in Table 8 for a maximum of a 50 ng injection or purging of BFB. Analysis must not begin until these criteria are met. These criteria must be met for each 12-hour time period. The 12-hour time period begins at the moment of injection of BFB.

10.4. Initial Calibration

10.4.1. A series of at least five initial calibration standards is prepared and analyzed for the target compounds and each surrogate compound. Six standards must be used for a quadratic least squares calibration. Suggested calibration levels for a 5 mL purge are: 5, 20, 50, 100, and 200 µg/L. Certain analytes are prepared at higher concentrations due to poor purge performance. Suggested calibration levels for a low level 5mL purge are 1, 5, 10, 20, and 40 µg/L. Again, some analytes are prepared at higher levels. Tables 2, 2A, and 4 list the calibration levels for each analyte. Other calibration levels and purge volumes may be used depending on the capabilities of the specific instrument. (For example, adequate sensitivity can be obtained by using a 5 mL purge volume to reach the same reporting limits that once required a 25 mL purge. The calibration levels will still be the same 1, 5, 10, 20, 40 µg/L.) However, the same purge volume must be used for calibration and sample analysis, and the low level standard must be at or below the reporting limit.

NOTE: For Method 8260C. Historically the surrogate compounds have been included in the multi-point initial calibration at variable concentrations in order to evaluate the linear response as with any target analyte. However, with improvements in instrumentation and more reliance on the autosampler, an option is available depending on the project-specific data quality requirements for allowing the autosampler (or using a manual technique) to spike the initial calibration standards with surrogates in the same manner as the samples are spiked. With this option the surrogate standards in the initial calibration can be averaged to develop a response factor and an effective one point calibration with the sole purpose to measure the surrogate recovery using the same concentration for each sample analysis. For this calibration option the surrogate linear response is less important, since multiple concentrations of surrogates are not being measured. Instead, the surrogate concentration remains constant throughout and the recovery of this known concentration can easily be attained without demonstrating if the response is linear. Under a second calibration option, the surrogates can be calibrated in the same manner as the target analytes, however, the laboratory should have the latitude to employ either option given the instrument system limitations and the ability to meet the project's data quality objectives.

10.4.2. It may be necessary to analyze more than one set of calibration standards to encompass all of the analytes required for same tests.

10.4.3. Internal standard calibration is used. The internal standards are listed in Table 5. Target compounds must reference the nearest internal standard. Each calibration standard is analyzed and the response factor (RF) for each compound is calculated using the area response of the characteristic ions against the concentration for each compound and internal standard. See Table 12 for a list of characteristic ions. See Equation 1, Section

12, for calculation of response factor.

10.4.4. For Method 8260B, the % RSD of the calibration check compounds (CCC) must be less than 30%. Refer to Table 11 for the CCCs. This criteria must be met before sample analysis begins.

10.4.4.1. Calibration Check Compound (CCC) (Method 8260B only)

10.4.4.1.1. CCCs are a representative group of compounds, which are used to evaluate initial calibrations and continuing calibrations. Relative percent difference for the initial calibration and % drift for the continuing calibration response factors are calculated and compared to the specified method criteria.

10.4.4.2. System Performance Check Compounds (SPCC) (Method 8260B only)

10.4.4.2.1 SPCCs are compounds, which are sensitive to system performance problems and are used to evaluate system performance and sensitivity. A response factor from the continuing calibration is calculated for the SPCC compounds and compared to the specified method criteria.

10.4.5. The average RF must be calculated for each compound. A system performance check is made prior to using the calibration curve. The five system performance check compounds (SPCC) are checked for a minimum average response factor. Refer to Table 9 for the SPCC compounds for Method 8260B and required minimum response factors. Refer to Table 10 for the recommended minimum average relative response factor criteria for initial and continuing calibration verification for Method 8260C.

10.4.6. Weighting of Data Points

10.4.6.1. In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason, it is preferable to increase the weighting of the lower concentration points. $1/\text{Concentration}^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and must be used if the data system has this capability. The Y-intercept is evaluated to determine calibration acceptability.

10.4.7. For any analyte with % RSD >15%, linear or quadratic curve fits may be used if the compounds have historically exhibited a non-linear response. The analyst must

consider instrument maintenance to improve the linearity of response. Nonlinear calibration models cannot be used to extend the calibration range for compounds that normally exhibit a linear response, but in a narrower calibration range. If the % RSD is > 15%, the analyst may drop the low or high in the ICAL, as long as a minimum of five points are maintained (six points for quadratic) and the quantitation range is adjusted accordingly. Otherwise, the coefficient of determination r^2 must be ≥ 0.990 . For Method 8260C, % RSD is $\pm 20\%$ for each target analyte.

10.4.8. If time remains in the 12-hour period initiated by the BFB injection before the initial calibration, samples may be analyzed. Otherwise, proceed to continuing calibration.

10.4.9. The calibration standards for the initial five-point calibration for low-level soils that are not preserved in sodium bisulfate (i.e., are preserved by freezing or not preserved) must be heated to 40°C for purging. Using this calibration curve for water samples is acceptable as long as all calibration, QC, and samples are also heated to 40°C. A separate five-point calibration must be prepared for analysis of low level soils that are preserved with sodium bisulfate. Low-level soils analysis requires the use of a closed vial autosampler such as the Varian Archon, O.I. 4552 or Tekmar Precept. Each standard for analysis of sodium bisulfate preserved samples is prepared by spiking the methanolic standard solution through the septum of a VOA vial containing 5 mL of water and 1g sodium bisulfate. The standards are heated to 40°C for purging. All low-level soil samples, standards, and blanks must also be heated to 40°C for purging.

10.4.10. Non-standard analytes are sometimes requested. For these analytes, it is acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five-point initial calibration. If the analyte is detected in any of the samples, a five-point initial calibration must be generated and the sample(s) re-analyzed for quantitation. However, if the analyte is not detected, the non-detect must be reported and no further action is necessary.

Note: This procedure must not be used for Ohio VAP samples.

10.4.11. Calibration accuracy is verified by analyzing a second source standard (ICV) immediately after the initial calibration. For Method 8260B, the recovery for CCC compounds must be $\leq 20\%$. The recovery for non-CCC compounds must be $\leq 50\%$ with an allowance of up to six compounds $> 50\%$.

10.4.11.1 For Method 8260C, the acceptance criteria is 70-130% for each target analyte.

10.5. Continuing Calibration. The initial calibration must be verified every 12 hours.

- 10.5.1. Continuing calibration begins with analysis of BFB as described in Section 10.3. If the system tune is acceptable, the continuing calibration standard(s) are analyzed. A midpoint calibration standard is used as the continuing calibration.
- 10.5.2. The RF data from the standards are compared with the average RF from the initial five-point calibration to determine the percent drift of the CCC compounds. The calculation is given in Equation 4, Section 12.3.4.
- 10.5.3. For Method 8260B, the % drift of the CCCs must be $\leq 20\%$ for the continuing calibration to be valid. The SPCCs are also monitored. The SPCCs must meet the criteria described in Table 9. In addition, the percent drift of all analytes must be $\leq 50\%$ with allowance for up to six target analytes to have percent drift $> 50\%$.
- 10.5.3.1. For Method 8260C, all compounds of interest must be verified at 20%.
- 10.5.3.2. Refer to Table 11 for specific Ohio VAP analytes.
- 10.5.4. If the CCCs and/or the SPCCs do not meet the criteria in Section 10.5.3 and Table 9, the system must be evaluated and corrective action must be taken. The BFB tune and continuing calibration must be acceptable before analysis begins. Extensive corrective action such as a different type of column will require a new initial calibration. For Method 8260C, any sample non-detects for an analyte that fails the SOP criteria low, must have a low level CCV (CCV at the RL) in the batch as a sensitivity demonstration. The criterion for a passing LLCCV is detection only, and a passing LLCCV allows non-detect samples to be reported without flagging.
- 10.5.5. Once the above criteria have been met, sample analysis may begin. **Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs.** Analysis may proceed until 12 hours from the injection of the BFB have passed. (A sample *desorbed* less than or equal to 12 hours after the BFB is acceptable.)

11. PROCEDURE

11.1. Procedural Variations

- 11.1.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation must be completely documented using a Nonconformance Memo and approved by a Supervisor or Group Leader. The Nonconformance Memo must be filed in the project file.

11.1.2. Any unauthorized deviations from this procedure must also be documented as a non-conformance with a cause and corrective action described. The laboratory may not deviate from the method for Ohio VAP samples.

11.2. Preliminary Evaluation

11.2.1. Where possible, samples are screened by headspace or GC/MS off-tune analysis to determine the correct aliquot for analysis. Alternatively, an appropriate aliquot can be determined from sample histories.

11.3. Sample Analysis Procedure

11.3.1. All analysis conditions for samples must be the same as for the continuing calibration standards (including purge time and flow, desorb time and temperature, column temperatures, multiplier setting etc.).

11.3.2. All samples must be analyzed as part of a batch. The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The batch also must contain an MS/MSD, an LCS, and a method blank. See Section 9.4 for method blank preparation.

11.3.2.1. If there is insufficient time in the 12-hour tune period to analyze 20 samples, the batch may be continued into the next tune period. However, if any re-tuning of the instrument is necessary, or if a period of greater than 24 hours from the preceding BFB tune has passed, a new batch must be started. For medium-level soils, the batch is defined at the sample preparation stage.

11.3.2.2. It is not necessary to re-analyze batch QC with re-analyses of samples. However, any reruns must be part of a valid batch.

11.3.3 Dilutions must be done just prior to the GC/MS analysis of the sample. Dilutions are made in a Luerlok syringe. Calculate the volume of reagent water required for the dilution. Fill the syringe with reagent water, compress the water to vent any residual air and adjust the water volume to the desired amount. Adjust the plunger to the mark and inject the proper aliquot of sample into the syringe. If the dilution required would use less than 1 μ L of sample, then serial dilutions must be made in volumetric flasks. Dilutions may also be prepared in a 40 mL vial. An appropriate amount of water is added to the vial. The sample is added using an appropriate syringe.

11.3.3.1 The diluted concentration is to be estimated to be in the upper half of the calibration range.

11.4. Methanol Extract Soils

11.4.1 Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 μ L for a 5 mL purge) methanolic extract (from Sections 8.5 or 8.6) to the syringe. If less than 1 μ L of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 1 μ L will be added to the water in the syringe. Refer to Section 17.2 for Michigan project requirements.

11.5. Liquid wastes that are soluble in methanol and insoluble in water.

11.5.1 Pipette 1 mL of the sample into a tared vial. Use a top-loading balance. Record the weight to the nearest 0.1g.

11.5.2 Quickly add 4 mL of methanol, then add 5 μ L of a 2500 μ g/mL surrogate spiking solution to bring the final volume to 5 mL. Cap the vial and shake for two minutes to mix thoroughly. For an MS/MSD or LCS, 4.9 mL of methanol, 5 μ L of a 2500 μ g/mL surrogate spiking solution, and 0.1 mL of matrix spike solution is used.

11.5.3 Rinse a gas-tight syringe with organic-free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 μ L for a 5 mL purge) methanolic extract (from Sections 8.5 or 8.6) to the syringe. If less than 5 μ L of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 1 μ L will be added to the water in the syringe.

11.6. Aqueous and low-level soil sample analysis (Purge and Trap units that sample directly from the VOA vial)

11.6.1 Units which sample from the VOA vial must be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.6.2 If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise, the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to be analyzed as soils.

11.6.3 Soil samples, which are preserved with sodium bisulfate, must be quantitated against a curve prepared with standards containing about the same amount of sodium bisulfate as the samples (1g in 5 mL).

11.6.4 Soil samples, which are preserved by freezing, must be allowed to thaw completely before sample analysis begins.

11.6.5 Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.7 Water Samples Not Directly Sampled from VOA Vials

11.7.1. All samples and standard solutions must be at ambient temperature before analysis.

11.7.2. Fill a syringe with the sample. If a dilution is necessary it may be made in the syringe if the sample aliquot is $\geq 5 \mu\text{L}$. Check and document the pH of the remaining sample.

11.7.3. Add 50 ng of each internal and surrogate standard. The internal standards and the surrogate standards may be mixed and added as one spiking solution (this results in a 10 $\mu\text{g/L}$ solution for a 5 mL sample). Inject the sample into the purging chamber. The internal and surrogate standards can be added automatically by the autosampler.

11.7.3.1. For TCLP samples, use 0.1 mL of TCLP leachate with 4 mL reagent water. (Note: TCLP reporting limits will be five times higher than the corresponding aqueous limits.)

11.7.4. Purge the sample for 11 minutes (trap must be below 35°C).

11.7.5. After purging is complete, desorb the sample, start the GC temperature program, and begin data acquisition. After desorption, bake the trap for approximately 3-10 minutes to condition it for the next analysis. When the trap is cool, it is ready for the next sample.

11.7.6. Desorb and bake time and temperature are optimized for the type of trap in use. The same conditions must be used for samples and standards.

11.8. *Low-Level Solids Analysis using discrete autosamplers, Methods 8260A and 5030A*

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated soil/sediment sample mixed with reagent water containing the surrogates and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.8.1. *Weigh out 5g (or other appropriate aliquot) of sample into a 40 mL vial. Record the weight to the nearest 0.1g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 0.5g. If the sample is contaminated with analytes such that a purge amount less than 0.5g is appropriate, use the medium level method. For the medium level method, add 5g soil to 5 mL methanol containing the surrogates, mix for two minutes, allow to settle, and store in a clean Teflon®-capped vial at 4°C until analysis. Analyze as described in Section 11.5.*

11.8.2 *Add 5 mL of organic free water to the VOA vial. Add surrogate/internal standard (and matrix spike solutions if required.). Add directly to the sample from Section 11.5.1.*

11.8.3. *The above steps must be performed rapidly and without interruption to avoid loss of volatile organics.*

11.9 Medium-Level Soil/Sediment and Waste Samples

11.9.1. Sediments/soils and waste that are insoluble in methanol.

11.9.1.1 Weigh 5 g (wet weight) into a tared vial. Use a top-loading balance. Record the weight to 0.1 gram. Do not discard any supernatant liquids.

11.9.1.2 Quickly add 5 mL of methanol, and 5µL of 2500 µg/mL surrogate spiking solution to bring the final volume of methanol to 5 mL. For an LCS or MS/MSD sample, add 4.9 mL of methanol, 5µL of surrogate spike solution, and 0.1 mL of matrix spike solution. Cap the vial and shake or vortex to mix thoroughly.

Note: Sections 11.9.1.1 and 11.9.1.2 must be performed rapidly and without interruption to avoid the loss of volatile organics.

11.10. Initial review and corrective actions

11.10.1. If the retention time for any internal standard in the continuing calibration changes by more than 0.5 minutes from the mid-level initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Re-analysis of samples analyzed while the system was malfunctioning is required.

11.10.2. If the internal standard response in the continuing calibration is more than 200% or less than 50% of the response in the mid-level of the initial calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Re-analysis of samples analyzed while the system was malfunctioning is required. Re-analysis must be undiluted if matrix interference is not observed.

11.10.2.1. Any samples that do not meet the internal standard criteria for the continuing calibration must be evaluated for validity. If the change in sensitivity is a matrix effect, the sample is re-analyzed to confirm. If the change in sensitivity is due to instrumental problems, all affected samples must be re-analyzed after the problem is corrected. For Ohio VAP projects, the laboratory will re-analyze any sample where the internal standard fails, and there is no evidence of matrix interference. If there is no matrix interference, the sample must be reanalyzed at the original dilution. If the internal standard is within criteria, report the second analysis. If the internal standard is still outside of criteria, the sample must be analyzed at a second dilution. If the internal standard still does not meet criteria, the sample must be diluted until the internal standard meets criteria. Multiple runs may be required..

11.11. Dilutions

11.11.1 If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution must be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be re-analyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

11.11.2 Guidance for Dilutions Due to Matrix

11.11.2.1 If the sample is initially run at a dilution and the baseline rise is less than half the height of the internal standards, or if individual non target peaks are less than twice the height of the internal standards, then the sample must be re-analyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement.

11.11.3 Reporting Dilutions

11.11.3.1 The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1 An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NIST Library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component, and (2) correspondence of the sample component and the standard component characteristic ions. See Table 12 for a list of the characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

12.1.1.1 The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same 12 hours as the sample.

12.1.1.2 The relative intensities of ions must agree to within $\pm 30\%$ between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.)

12.1.2 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst, the identification is correct, then the analyst must report that identification and proceed with quantitation.

12.2. Tentatively Identified Compounds (TICs)

12.2.1. If the client requests components not associated with the calibration standards, a search of the NIST library may be made for the purpose of tentative identification. Guidelines are:

12.2.1.1. Relative intensities of major ions in the reference spectrum (ions $> 10\%$ of the most abundant ion) must be present in the sample spectrum.

12.2.1.2. The relative intensities of the major ions must agree to within 20%. (Example: If an ion shows an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

12.2.1.3. Molecular ions present in the reference spectrum must be present in the

sample spectrum.

12.2.1.4. Ions present in the sample spectrum but not in the reference spectrum must be reviewed for possible background contamination or presence of coeluting compounds.

12.2.1.5. Ions present in the reference spectrum but not in the sample spectrum must be reviewed for possible subtraction from the spectrum because of background contamination or coeluting peaks. (Data system reduction programs can sometimes create these discrepancies.)

12.2.1.6. Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual inspection of the sample with the nearest library searches must the analyst assign a tentative identification.

12.3. Calculations

12.3.1. Response Factor (RF)

Equation 1

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specific internal standard

C_{is} = Concentration of the specific internal standard, ng

C_x = Concentration of the compound being measured, ng

12.3.2. Standard Deviation (SD)

Equation 2

$$SD = \sqrt{\sum_{i=1}^N \frac{(X_i - \bar{X})^2}{N - 1}}$$

Where:

X_i = Value of X at i through N

N = Number of points

\bar{X} = Average value of X_i

12.3.3. Percent Relative Standard Deviation (%RSD)

Equation 3

$$\%RSD = \frac{\text{Standard Deviation}}{\bar{RF}_i} \times 100$$

\bar{RF}_i = Mean of RF values in the curve

12.3.4. Percent Drift Between the Initial Calibration and the Continuing Calibration

Equation 4

$$\% \text{ Drift} = \frac{C_{\text{expecte}} - C_{\text{found}}}{C_{\text{expecte}}} \times 100$$

Where:

C_{expecte} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.3.5. Target Compound and Surrogate Concentrations

12.3.5.1 Concentrations in the sample may be determined from linear or second order (quadratic) curve fitted to the initial calibration points, or from the average response factor of the initial calibration points. Average response factor may only be used when the % RSD of the response factors in the initial calibration is $\leq 15\%$.

12.3.5.2 Calculation of Concentration Using Average Response Factors

Equation 5

$$\text{Concentration } \mu\text{g} / \text{L} = \frac{x}{RF}$$

12.3.5.3 Calculation of Concentration using Linear Fit

Equation 6

$$\text{Concentration } \mu\text{g} / \text{L} = A + Bx$$

12.3.5.4. Calculation of Concentration Using Quadratic Fit

Equation 7

$$\text{Concentration } \mu\text{g} / \text{L} = A + Bx + Cx^2$$

Where:

X is defined in Equations 8, 9, and 10

A is a constant defined by the intercept

B is the slope of the curve

C is the curvature

12.3.5.5. Calculation of x for Water and water-miscible waste:

Equation 8

$$x = \frac{(A_x)(I_s)(D_f)}{(A_{is})(V_o)}$$

Where:

$X = \mu\text{g/L}$

A_x = Area of characteristic ion for the compound being measured
(secondary ion quantitation is allowed only when there are
sample interferences with the primary ion)

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard added in ng

$$\text{Dilution Factor} = D_f = \frac{\text{Total volume purged (mL)}}{\text{Volume of original sample used (mL)}}$$

V_o = Volume of water purged, mL

12.3.5.6. Calculation of x for Medium level soils:

Equation 9

$$x = \frac{(A_x)(I_s)(V_t)(1000)(D_f)}{(A_{is})(V_a)(W_s)(D)}$$

Where:

X = ug/kg

A_x , I_s , D_f , A_{is} , same as for water

V_t = Volume of total extract, mL

V_a = Volume of extract added for purging, μL

W_s = Weight of sample extracted, g

$$D = \frac{100 - \% \text{moisture}}{100}$$

12.3.5.7. Calculation of x for Low level soils:

Equation 10

$$x = \frac{(A_x)(I_s)}{(A_{is})(W_s)(D)}$$

Where:

X = ug/kg

A_x , I_s , A_{is} , same as for water

D = as for medium level soils

W_s = Weight of sample added to the purge vessel, g

12.3.5.8. Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x = Area in the total ion chromatogram for the compound being measured

A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference

$RF = 1$

In other words, the concentration is equal to x as defined in Equations 8, 9, and 10.

12.3.6. MS/MSD Recovery

Equation 11

$$\text{Matrix Spike Recovery, \%} = \frac{SSR - SR}{SA} \times 100$$

Where,

SSR = Spike Sample result

SR = Sample Result

SA = Spiked amount

12.3.7. Relative % Difference calculation for the MS/MSD:

Equation 12

$$RPD = \frac{|\text{MSR} - \text{MSDR}|}{\frac{1}{2}(\text{MSR} + \text{MSDR})} \times 100$$

Where:

RPD = Relative percent difference

MSR = Matrix spike result

MSDR = Matrix spike duplicate result

12.4 Additional equations and calculations are listed in the following SOPs: Calibration Curves

(General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Method Detection Limit

13.1.1. Generally, each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is defined in QA SOPs NC-QA-021 and CA-Q-S-006. When non-standard compounds are analyzed at client request, lesser requirements are possible with client agreement. At a minimum, a standard at the reporting limit must be analyzed to demonstrate the capability of the method. The non-standard compound must be detected in the reporting limit standard to be acceptable.

13.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client.

13.2. Initial Demonstration

13.2.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.3. Training Qualification

13.3.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Specific training requirements are outlined in the Quality Assurance Manual.

13.3.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. 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".

15. WASTE MANAGEMENT

- 15.1. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.
- 15.2. All waste will be disposed of in accordance with Federal, State, and Local laws and 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 Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for “Waste Management and Pollution Prevention”.
- 15.3. The following waste streams are produced when this method is carried out.
 - 15.3.1. **Acidic material from the auto-sampler:** Waste stream must be collected and neutralized before discharge to a sewer system if the pH is less than 5.
 - 15.3.2. **Methanol waste from rinses and standards:** Methanol waste is discarded as a flammable liquid in a solvent waste container identified as “Flammable Liquid Waste”.
 - 15.3.3. **All samples including purged and extracted soils and waters:** Samples are collected in boxes and removed from the lab to storage. The Waste Coordinator handles crushing the vials and proper disposal.
 - 15.3.4. **Solid samples** - Stirbars are removed from the sample. The contents of the vial are poured into a beaker, and the soil allowed to settle out. The soil is disposed of in the solid waste container.

16. REFERENCES

16.1. References

- 16.1.1. SW846, *Test Methods for Evaluating Solid Waste*, Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260B, Update III, December 1996

- 16.1.2. SW846, *Test Methods for Evaluating Solid Waste*, Third Edition, Gas Chromatography/Mass Spectrometry for Volatile Organics, Method 8260A, Update II, September 1994
- 16.1.3. SW846, *Test Methods for Evaluating Solid Waste*, Third Edition, Purge-and-Trap for Aqueous Samples, Method 5030B, Rev 2, December 1996
- 16.1.4. SW846, *Test Methods for Evaluating Solid Waste*, Third Edition, Purge-and-Trap for Aqueous Samples, Method 5030A, Rev 1, July 1992
- 16.1.5. SW846, *Test Methods for Evaluating Solid Waste*, Third Edition, Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Method 5035, Rev 0, December 1996
- 16.1.6 SW846, Test Methods for Evaluating Solid Waste Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, Method 5035A, Draft Revision 1, July 2002
- 16.1.7 SW846, Test Methods for Evaluation Solid Waste, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Method 8260C, Revision 3, August 2006.
- 16.1.7 [TestAmerica Canton Quality Assurance Manual \(QAM\)](#), current version
- 16.1.8 TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [Canton Facility Addendum and Contingency Plan](#), current version
- 16.1.9 Corporate Quality Management Plan (CQMP), current version

16.1.10 Revision History

Historical File:	Revision 2.0: 12/15/97	Revision 0: 06/30/08 (NC-MS-019)
(formerly CORP-MS-0002NC)	Revision 2.1: 03/06/00	Revision 1: 01/07/09
	Revision 2.2: 11/28/00	Revision 2: 02/17/12
	Revision 2.3: 05/23/01	
	Revision 2.4: 09/27/04	
	Revision 2.5: 04/03/07	

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, [QA-003](#)

16.2.2. Glassware Washing, [NC-QA-014](#)

16.2.3. Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)

16.2.4. Method Detection Limits and Instrument Detection Limits [NC-QA-021](#) and [CA-Q-S-006](#)

16.2.5. Supplemental Practices for DoD Project Work, [NC-QA-016](#)

16.2.6. Standards and Reagents, [NC-QA-017](#)

16.2.7. Laboratory Holding Blanks, [NC-QA-020](#)

16.2.8. Selection of Calibration Points, [CA-T-P-002](#)

16.2.9. Calibration Curves (General), [CA-Q-S-005](#)

16.2.10. Acceptable Manual Integration Practices, [CA-Q-S-002](#)

17. MISCELLANEOUS

17.1. Modifications from the reference method

17.1.1. A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2. The quantitation and qualifier ions for some compounds have been changed from those recommended in SW846 in order to improve the reliability of qualitative identification.

17.2. The following are protocols that must be followed to achieve the lower reporting limits required when analyzing Michigan projects.

17.2.1. Modify Sections 8.5.4 and 8.6.8 (add 5 uL of 2500 ug/mL surrogate solution for a nominal 10g sample).

17.2.2. Modify Sections 8.5.5 and 8.6.9 (add 200 uL of 25 ug/mL spike solution for a

nominal 10g sample).

17.2.3 Modify Sections 8.5.6 and 8.6.10 (add 200 uL of 25 ug/mL spike solution for a nominal 10g sample).

17.2.4 Michigan reporting limits for methanol preserved soils are achieved by injecting 100 uL of the methanol extract in a 5 mL purge. The instrument is calibrated using the recommended calibration range for water of 0.5 ug/L to 100 ug/L. Some analytes are prepared at higher concentrations.

Table 1 - TestAmerica Reporting Limits

Compound	CAS Number	Reporting Limits ¹				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
Dichlorodifluoromethane	75-71-8	5	1	5	250	250
Chloromethane	74-87-3	5	1	5	250	250
Bromomethane	74-83-9	5	1	5	250	250
Vinyl chloride	75-01-4	5	1	5	250	250
Chloroethane	75-00-3	5	1	5	250	250
Trichlorofluoromethane	75-69-4	5	1	5	250	250
Acrolein	107-02-8	100	20	100	5,000	5,000
Acetone	67-64-1	20	10	20	1,000	1,000
Trichlorotrifluoroethane	76-13-1	5	1	5	250	250
Iodomethane	74-88-4	5	1	5	250	250
Carbon disulfide	75-15-0	5	1	5	250	250
Methylene chloride	75-09-2	5	1	5	250	250
tert-Butyl alcohol	75-65-0	200	50	200	10,000	10,000
1,1-Dichloroethene	75-35-4	5	1	5	250	250
1,1-Dichloroethane	75-34-3	5	1	5	250	250
Trans-1,2-Dichloroethene	156-60-5	5.0	1.0	5.0	250	250
Acrylonitrile	107-13-1	100	20	100	5,000	5,000
Methyl tert-butyl ether (MTBE)	1634-04-4	5	1	5	250	250
Hexane	110-54-3	5	1	5	250	250
cis-1,2-Dichloroethene	156-59-2	5	1	5	250	250
1,2-Dichloroethene (Total)	540-59-0	10	2	10	500	500
Tetrahydrofuran	109-99-9	20	5	20	1,000	1,000
Chloroform	67-66-3	5	1	5	250	250
1,2-Dichloroethane	107-06-2	5	1	5	250	250
Dibromomethane	74-95-3	5	1	5	250	250
2-Butanone	78-93-3	20	5	20	1,000	1,000
1,4-Dioxane	123-91-1	500	200	500	25,000	25,000
1,1,1-Trichloroethane	71-55-6	5	1	5	250	250
Carbon tetrachloride	56-23-5	5	1	5	250	250
Bromodichloromethane	75-27-4	5	1	5	250	250
1,2-Dichloropropane	78-87-5	5	1	5	250	250
cis-1,3-Dichloropropene	10061-01-5	5	1	5	250	250
Trichloroethene	79-01-6	5	1	5	250	250
Dibromochloromethane	124-48-1	5	1	5	250	250
1,2-Dibromoethane	106-93-4	5	1	5	250	250
1,2,3-Trichloropropane	96-18-4	5	1	5	250	250

Table 1 - TestAmerica Reporting Limits

Compound	CAS Number	Reporting Limits ¹				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
1,1,2-Trichloroethane	79-00-5	5	1	5	250	250
Benzene	71-43-2	5	1	5	250	250
Ethylmethacrylate	97-63-2	5	1	5	250	250
Trans-1,3-Dichloropropene	10061-02-6	5	1	5	250	250
Bromoform	75-25-2	5	1	5	250	250
4-Methyl-2-pentanone	108-10-1	20	5	20	1000	1,000
2-Hexanone	591-78-6	20	5	20	1000	1,000
Tetrachloroethene	127-18-4	5	1	5	250	250
Toluene	108-88-3	5	1	5	250	250
1,1,2,2-Tetrachloroethane	79-34-5	5	1	5	250	250
2-Chloroethyl vinyl ether	110-75-8	N/A ²	N/A	50	1000	1,000
Vinyl acetate	108-05-4	10	2	10	500	500
Chlorobenzene	108-90-7	5	1	5	250	250
Ethylbenzene	100-41-4	5	1	5	250	250
Styrene	100-42-5	5	1	5	250	250
t-1,4-Dichloro-2-butene	110-57-6	5	1	5	250	250
m and p Xylenes		10	2	10	500	500
o-xylene	95-47-6	5.0	1	5	250	250
Total xylenes	1330-20-7	10	2	10	500	500
1,3-Dichlorobenzene	541-73-1	5	1	5	250	250
1,4-Dichlorobenzene	106-46-7	5	1	5	250	250
1,2-Dichlorobenzene	95-50-1	5	1	5	250	250
2,2-Dichloropropane	590-20-7	5	1	5	250	250
Bromochloromethane	74-97-5	5	1	5	250	250
1,1-Dichloropropene	563-58-6	5	1	5	250	250
Bromodichloromethane	75-27-4	5	1	5	250	250
1,2-Dichloropropane	78-87-5	5	1	5	250	250
1,3-Dichloropropane	142-28-9	5	1	5	250	250
Isopropylbenzene	98-82-8	5	1	5	250	250
Bromobenzene	108-86-1	5	1	5	250	250
n-Propylbenzene	103-65-1	5	1	5	250	250
2-Chlorotoluene	95-49-8	5	1	5	250	250
4-Chlorotoluene	106-43-4	5	1	5	250	250
1,3,5-Trimethylbenzene	108-67-8	5	1	5	250	250
Tert-Butylbenzene	98-06-6	5	1	5	250	250
1,2,4-Trimethylbenzene	95-63-6	5	1	5	250	250
Sec-butylbenzene	135-98-8	5	1	5	250	250

Table 1 - TestAmerica Reporting Limits

Compound	CAS Number	Reporting Limits ¹				
		5 mL Water µg/L	Low Level 5 mL water µg/L	Low soil µg/kg	8260B/ 5035 Soil ug/kg	8260A 5030A Med Level Soil µg/kg
4-Isopropyltoluene	99-87-6	5	1	5	250	250
n-Butylbenzene	104-51-8	5	1	5	250	250
1,2,4-Trichlorobenzene	120-82-1	5	1	5	250	250
Napthalene	91-20-3	5	1	5	250	250
Hexachlorobutadiene	87-68-3	5	1	5	250	250
1,2,3-Trichlorobenzene	87-61-6	5	1	5	250	250
Acetonitrile	75-05-8	100	20	100	5000	500
Cyclohexane	110-82-7	10	1	10	500	500
Methyl Acetate	79-20-9	10	10	10	500	500
Methyl cyclohexane	108-87-2	10	1	10	500	500

¹ Reporting limits listed for soil/sediment are based on wet weight. The reporting limits calculated by the laboratory for soil/sediment, calculated on dry weight basis, will be higher.

² 2-Chloroethyl vinyl ether cannot be reliably recovered from acid preserved samples

Table 2 - TestAmerica Primary Standard Calibration Levels, 5 mL purge Solid

Compound	Calibration Level ug/kg				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2-Dichloroethane-d4 (Surrogate)	5	10	50	100	200
Toluene-d8 (Surrogate)	5	10	50	100	200
4-Bromofluorobenzene (Surrogate)	5	10	50	100	200
Dichlorodifluoromethane	5	10	50	100	200
Chloromethane	5	10	50	100	200
Bromomethane	5	10	50	100	200
Vinyl chloride	5	10	50	100	200
Chloroethane	5	10	50	100	200
Trichlorofluoromethane	5	10	50	100	200
Acrolein	50	100	500	1000	2000
Acetone	10	20	100	200	400
Trichlorotrifluoroethane	5	10	50	100	200
Iodomethane	5	10	50	100	200
Carbon disulfide	5	10	50	100	200
Methylene chloride	5	10	50	100	200
tert-Butyl alcohol	100	200	1,000	2,000	4,000
1,1-Dichloroethene	5	10	50	100	200

Table 2 - TestAmerica Primary Standard Calibration Levels, 5 mL purge Solid

Compound	Calibration Level ug/kg				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,1-Dichloroethane	5	10	50	100	200
trans-1,2-Dichloroethene	5	10	50	100	200
Acrylonitrile	50	100	500	1000	2000
Methyl <i>tert</i> -butyl ether (MTBE)	5	10	50	100	200
Hexane	5	10	50	100	200
cis-1,2-Dichloroethene	5	10	50	100	200
Tetrahydrofuran	5	10	50	100	200
Chloroform	5	10	50	100	200
1,2-Dichloroethane	5	10	50	100	200
Dibromomethane	5	10	50	100	200
2-Butanone	10	20	100	200	400
1,4-Dioxane	250	500	2,500	5,000	10,000
1,1,1-Trichloroethane	5	10	50	100	200
Carbon tetrachloride	5	10	50	100	200
Bromodichloromethane	5	10	50	100	200
1,2-Dichloropropane	5	10	50	100	200
cis-1,3-Dichloropropene	5	10	50	100	200
Trichloroethene	5	10	50	100	200
Dibromochloromethane	5	10	50	100	200
1,2-Dibromoethane	5	10	50	100	200
1,2,3-Trichloropropane	5	10	50	100	200
Acetonitrile	50	100	500	1000	2000
1,1,2-Trichloroethane	5	10	50	100	200
Benzene	5	10	50	100	200
Ethylmethacrylate	5	10	50	100	200
trans-1,3-Dichloropropene	5	10	50	100	200
Bromo form	5	10	50	100	200
4-Methyl-2-pentanone	10	20	100	200	400
2-Hexanone	10	20	100	200	400
Tetrachloroethene	5	10	50	100	200
Toluene	5	10	50	100	200
1,1,2,2-Tetrachloroethane	5	10	50	100	200
2-Chloroethyl vinyl ether	10	20	100	200	400
Vinyl acetate	5	10	50	100	200
Chlorobenzene	5	10	50	100	200
Ethylbenzene	5	10	50	100	200
Styrene	5	10	50	100	200
t-1,4-Dichloro-2-butene	5	10	50	100	200
m and p Xylenes	10	20	100	200	400
o-xylene	5	10	50	100	200

Table 2 - TestAmerica Primary Standard Calibration Levels, 5 mL purge Solid

Compound	Calibration Level ug/kg				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,3-Dichlorobenzene	5	10	50	100	200
1,4-Dichlorobenzene	5	10	50	100	200
1,2-Dichlorobenzene	5	10	50	100	200
2,2-Dichloropropane	5	10	50	100	200
Bromochloromethane	5	10	50	100	200
1,1-Dichloropropene	5	10	50	100	200
Bromodichloromethane	5	10	50	100	200
1,2-Dichloropropane	5	10	50	100	200
1,3-Dichloropropane	5	10	50	100	200
Isopropylbenzene	5	10	50	100	200
Bromobenzene	5	10	50	100	200
n-Propylbenzene	5	10	50	100	200
2-Chlorotoluene	5	10	50	100	200
4-Chlorotoluene	5	10	50	100	200
1,3,5-Trimethylbenzene	5	10	50	100	200
tert-Butylbenzene	5	10	50	100	200
1,2,4-Trimethylbenzene	5	10	50	100	200
sec-butylbenzene	5	10	50	100	200
4-Isopropyltoluene	5	10	50	100	200
n-Butylbenzene	5	10	50	100	200
1,2,4-Trichlorobenzene	5	10	50	100	200
Napthalene	5	10	50	100	200
Hexachlorobutadiene	5	10	50	100	200
1,2,3-Trichlorobenzene	5	10	50	100	200

Table 2A - TestAmerica Primary Standard Calibration Levels, Low Level ¹(Water)

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
Dibromofluoromethane (Surrogate)	1	2	10	20	40
1,2-Dichloroethane-d4 (Surrogate)	1	2	10	20	40
Toluene-d8 (Surrogate)	1	2	10	20	40
Bromofluorobenzene (Surrogate)	1	2	10	20	40
Dichlorodifluoromethane	1	2	10	20	40
Chloromethane	1	2	10	20	40
Vinyl Chloride	1	2	10	20	40
Bromomethane	1	2	10	20	40
Chloroethane	1	2	10	20	40
Trichlorofluoromethane	1	2	10	20	40
Acrolein	10	20	100	200	400
Acetone	2	4	20	40	80
1,1-Dichloroethene	1	2	10	20	40
Trichlorotrifluoroethane	1	2	10	20	40
Iodomethane	1	2	10	20	40
Carbon Disulfide	1	2	10	20	40
Methylene Chloride	1	2	10	20	40
Acetonitrile	10	20	100	200	400
Acrylonitrile	10	20	100	200	400
Methyl tert-butyl ether	1	2	10	20	40
trans-1,2-Dichloroethene	1	2	10	20	40
Hexane	1	2	10	20	40
Vinyl acetate	1	2	10	20	40
1,1-Dichloroethane	1	2	10	20	40
tert-Butyl Alcohol	20	40	200	400	800
2-Butanone	2	4	20	40	80
cis-1,2-dichloroethene	1	2	10	20	40
2,2-Dichloropropane	1	2	10	20	40
Bromochloromethane	1	2	10	20	40
Chloroform	1	2	10	20	40
Tetrahydrofuran	1	2	10	20	40
1,1,1-Trichloroethane	1	2	10	20	40
1,1-Dichloropropene	1	2	10	20	40
Carbon Tetrachloride	1	2	10	20	40
1,2-Dichloroethane	1	2	10	20	40
Benzene	1	2	10	20	40
Trichloroethene	1	2	10	20	40
1,2-Dichloropropane	1	2	10	20	40

Table 2A - TestAmerica Primary Standard Calibration Levels, Low Level ¹(Water)

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,4-Dioxane	50	100	500	1000	2000
Dibromomethane	1	2	10	20	40
Bromodichloromethane	1	2	10	20	40
2-Chloroethyl vinyl ether	2	4	20	40	80
cis-1,3-Dichloropropene	1	2	10	20	40
4-Methyl-2-pentanone	2	4	20	40	80
Toluene	1	2	10	20	40
trans-1,3-Dichloropropene	1	2	10	20	40
Ethyl Methacrylate	1	2	10	20	40
1,1,2-Trichloroethane	1	2	10	20	40
1,3-Dichloropropane	1	2	10	20	40
Tetrachloroethene	1	2	10	20	40
2-Hexanone	2	4	20	40	80
Dibromochloromethane	1	2	10	20	40
1,2-Dibromoethane	1	2	10	20	40
Chlorobenzene	1	2	10	20	40
1,1,1,2-Tetrachloroethane	1	2	10	20	40
Ethylbenzene	1	2	10	20	40
m + p-Xylene	2	4	20	40	80
Xylene-o	1	2	10	20	40
Styrene	1	2	10	20	40
Bromoform	1	2	10	20	40
Isopropylbenzene	1	2	10	20	40
1,1,2,2-Tetrachloroethane	1	2	10	20	40
1,4-Dichloro-2-butene	1	2	10	20	40
1,2,3-Trichloropropane	1	2	10	20	40
Bromobenzene	1	2	10	20	40
n-Propylbenzene	1	2	10	20	40
2-Chlorotoluene	1	2	10	20	40
1,3,5-Trimethylbenzene	1	2	10	20	40
4-Chlorotoluene	1	2	10	20	40
tert-Butylbenzene	1	2	10	20	40
1,2,4-Trimethylbenzene	1	2	10	20	40
sec-Butylbenzene	1	2	10	20	40
4-Isopropyltoluene	1	2	10	20	40
1,3-Dichlorobenzene	1	2	10	20	40
1,4-Dichlorobenzene	1	2	10	20	40
n-Butylbenzene	1	2	10	20	40
1,2-Dichlorobenzene	1	2	10	20	40
1,2-Dibromo-3-chloropropane	1	2	10	20	40

Table 2A - TestAmerica Primary Standard Calibration Levels, Low Level ¹(Water)

Compound	Calibration Level ug/L				
	Level 1	Level 2	Level 3	Level 4	Level 5
1,2,4-Trichlorobenzene	1	2	10	20	40
Hexachlorobutadiene	1	2	10	20	40
Naphthalene	1	2	10	20	40
1,2,3-Trichlorobenzene	1	2	10	20	40
Cyclohexane	1	2	10	20	40
Methyl Acetate	2	4	20	40	80
Methylcyclohexane	1	2	10	20	40
1,3,5-Trichlorobenzene	1	2	10	20	40

¹ 25 mL purge samples analyzed at 5 mL purge on more sensitive equipment.

Table 3 - TestAmerica Appendix IX Standard and Reporting Limits, 5 mL purge

Compound	CAS Number	Reporting Limits			
		5 mL Water µg/L	Low Level 5mL purge water µg/L	Low Soil µg/kg	Medium Soil µg/mL
Allyl Chloride	107-05-1	10	2	10	500
Dichlorofluoromethane	75-43-4	10	2	10	500
Isopropyl ether	108-20-3	10	2	10	500
Chloroprene	126-99-8	5	1	5	250
n-Butanol	71-36-3	200	50	200	10,000
Propionitrile	107-12-0	20	4	20	1000
Methacrylonitrile	126-98-7	5	1	5	250
Isobutanol	78-83-1	200	50	200	10,000
Methyl methacrylate	80-62-6	5	1	5	250
1,1,1,2-Tetrachloroethane	630-20-6	5	1	5	250
1,2-Dibromo -3-chloropropane	96-12-8	10	2	10	500
Ethyl ether	60-29-7	10	2	10	500
Ethyl Acetate	141-78-6	20	4	20	1,000
2-Nitropropane	79-46-9	10	4	10	500
Cyclohexanone	108-94-1	50	20	50	2500
Isopropylbenzene	98-82-8	5	1	5	250
2-Methylnaphthalene (Michigan only)	91-57-6	25	5	10	1250

Table 4

Recommended TestAmerica Appendix IX Standard Calibration Levels, µg/kg

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
Allyl Chloride	1	5	10	20	40
Dichlorofluoromethane	1	5	10	20	40
Isopropyl ether	5	25	50	100	200
Chloroprene	1	5	10	20	40
n-Butanol	20	100	200	400	800
Propionitrile	2	10	20	40	80
Methacrylonitrile	1	5	10	20	40
Isobutanol	20	100	200	400	800
Methyl methacrylate	1	5	10	20	40
Ethyl ether	1	5	10	20	40
Ethyl Acetate	2	10	20	40	80
2-Nitropropane	2	10	20	40	80
Cyclohexanone	10	50	100	200	400
2-Methylnaphthalene (Michigan only)	2	10	20	40	80
Ethyl tert-butyl ether	1	5	10	20	40
tert-Amyl methyl ether	1	5	10	20	40
1,2,3-Trimethylbenzene	1	5	10	20	40
2-Methylnaphthalene (Low Level Soil)	10	20	100	200	400

Table 5 - Internal Standards

Compound	Standard Concentration µg/mL (may vary per matrix)	Quantitation ion
Fluorobenzene	50 – 250	96
Chlorobenzene-d5	50 – 250	117
1,4-Dichlorobenzene-d4	50 – 250	152

Notes:

- 1) Except for medium level soils, the surrogate and internal standards may be combined in

one solution.

Table 6 - Surrogate Standards

Surrogate Compounds	Standard Concentration µg/mL (may vary per matrix)
1,2-Dichloroethane-d ₄	50 – 250
Dibromofluoromethane (not required for Method 8260C)	50 – 250
Toluene-d ₈	50 - 250
4-Bromofluorobenzene	50 – 250

Notes:

- 1) Except for medium level soils, the surrogate and internal standards may be combined in one solution.
- 2) Recovery limits for surrogates are generated from historical data and are maintained by the QA Dept.
- 3) There is no corrective action for Dibromofluoromethane for Method 8260C.

Table 7 - Matrix Spike / LCS Compounds

Compound	Standard Concentration µg /mL
1,1,1-Trichloroethane	50 – 250
1,1,2,2-Tetrachloroethane	50
1,1,2-Trichloro-1,2,2-trifluoroethane	50
1,1,2-Trichloroethane	50
1,1-Dichloroethane	50
1,1-Dichloroethene	50
1,1-Dichloropropene	50
1,2,3-Trichlorobenzene	50
1,2,3-Trichloropropane	50
1,2,4-Trichlorobenzene	50
1,2,4-Trimethylbenzene	50
1,2-Dibromo -3-chloropropane	50
1,2-Dibromoethane	50
1,2-Dichlorobenzene	50
1,2-Dichloroethane	50
1,2-Dichloroethene (total)	100
1,2-Dichloropropane	50
1,3,5-Trimethylbenzene	50
1,3-Dichlorobenzene	50
1,3-Dichloropropane	50
1,4-Dichlorobenzene	50
2,2-Dichloropropane	50
2-Butanone	50
2-Chloroethyl Vinyl Ether	100 – 500
2-Chlorotoluene	50
2-Hexanone	50
4-Chlorotoluene	50
4-Methyl-2-pentanone	50
Acetone	50
Acetonitrile	500 – 2500
Acrolein	500
Acrylonitrile	100 – 500
Benzene	50
Bromobenzene	50
Bromochloromethane	50
Bromodichloromethane	50
Bromoform	50
Bromomethane	50
Carbon disulfide	50
Carbon tetrachloride	50
Chlorobenzene	50
Chloroethane	50

Table 7 - Matrix Spike / LCS Compounds

Compound	Standard Concentration µg /mL
Chloroform	50
Chloromethane	50
cis-1,2-Dichloroethene	50
cis-1,3-Dichloropropene	50
Cyclohexane	50
Dibromochloromethane	50
Dibromomethane	50
Dichlorodifluoromethane	50
Ethylbenzene	50
Hexachlorobutadiene	50
Iodomethane	50
Isopropylbenzene	50
Isopropylether	50
Methyl acetate	50
Methyl tert-butyl ether (MTBE)	50
Methylcyclohexane	50
Methylene chloride	50
Naphthalene	50
n-Butylbenzene	50
n-Hexane (Ohio VAP only)	50
n-Propylbenzene	50
p-Isopropyltoluene	50
sec-Butylbenzene	50
Styrene	50
tert-Butylbenzene	50
Tetrachloroethene	50
Toluene	50
trans-1,2-Dichloroethene	50
trans-1,2-Dichloroethene	50
trans-1,3-Dichloropropene	50
Trichloroethene	50
Trichlorofluoromethane	50
Vinyl Acetate	50
Vinyl chloride	50
Xylenes (total)	150 – 750

- Notes: 1) 5 µL of the standard is added to the LCS or matrix spiked sample. This results in a concentration of each spike analyte in the sample of 50µg/L for a 5 mL purge or 10 µg/L for a 25 mL purge.
- 2) Recovery and precision limits for LCS and MS/MSD are generated from historical data and are maintained by QA Dept.

Table 8 - BFB Key Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15% to 40% of Mass 95
75	30% to 60% of Mass 95
95	Base Peak, 100% Relative Abundance
96	5% to 9% of Mass 95
173	Less Than 2% of Mass 174
174	Greater Than 50% of Mass 95
175	5% to 9% of Mass 174
176	Greater Than 95%, But Less Than 101% of Mass 174
177	5% to 9% of Mass 176

Table 9 - SPCC Compounds and Minimum Response Factors for Method 8260B

Compound	Methods 8260B and 8260A Min. RF
Chloromethane	0.100
1,1-Dichloroethane	0.100
Bromoform	0.100
1,1,2,2-Tetrachloro ethane	0.300
Chlorobenzene	0.300

Table 10 - Method 8260C. Recommended Average Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification		
Volatile Compound	Minimum Response Factor	Typical Response Factor
Dichlorodifluoromethane	0.100	0.327
Chloromethane	0.100	0.537
Vinyl chloride	0.100	0.451
Bromomethane	0.100	0.255
Chloroethane	0.100	0.254
Trichlorofluoromethane	0.100	0.426
1,1-Dichloroethene	0.100	0.313
1,1,2-Trichloro-1,2,2-trifluoroethane	0.100	0.302
Acetone	0.100	0.151
Carbon disulfide	0.100	1.163
Methyl Acetate	0.100	0.302
Methylene chloride	0.100	0.380
trans-1,2-Dichloroethene	0.100	0.351
cis-1,2-dichloroethene	0.100	0.376
Methyl tert-Butyl Ether	0.100	0.847
1,1-Dichloroethane	0.200	0.655
2-Butanone	0.100	0.216
Chloroform	0.200	0.557
1,1,1-Trichloroethane	0.100	0.442
Cyclohexane	0.100	0.579
Carbon tetrachloride	0.100	0.353
Benzene	0.500	1.368
1,2-Dichloroethane	0.100	0.443
Trichloroethene	0.200	0.338
Methylcyclohexane	0.100	0.501
1,2-Dichloropropane	0.100	0.382
Bromodichloromethane	0.200	0.424
cis-1,3-Dichloropropene	0.200	0.537
trans-1,3-Dichloropropene	0.100	0.515
4-Methyl-2-pentanone	0.100	0.363
Toluene	0.400	1.577
1,1,2-Trichloroethane	0.100	0.518
Tetrachloroethene	0.200	0.606
2-Hexanone	0.100	0.536
Dibromochloromethane	0.100	0.652
Styrene	0.300	1.916
Bromoform	0.100	0.413
Isopropylbenzene	0.100	2.271
1,1,2,2-Tetrachloroethane	0.300	0.782
1,3-Dichlorobenzene	0.600	1.408

Table 10 - Method 8260C: Recommended Minimum Relative Response Factor Criteria for Initial and Continuing Calibration Verification (cont'd)

Volatile Compound	Minimum Response Factor	Typical Response Factor
1,4-Dichlorobenzene	0.500	1.427
1,2-Dichlorobenzene	0.400	1.332
1,2-Dibromo -3-chloropropane	0.050	0.129
1,2,4-Trichlorobenzene	0.200	0.806

Table 11 - CCC Compounds for Method 8260B

Compound	Max. %RSD from Initial Calibration	Max. %D for continuing calibration
Vinyl Chloride	30	20
1,1-Dichloroethene	30	20
Chloroform	30	20
1,2-Dichloropropane	30	20
Toluene	30	20
Ethylbenzene	30	20
n-Hexane (Ohio VAP only)	30	20

Table 12 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
1,2-Dichloroethane-d ₄ (Surrogate)	65	102	
Dichlorodifluoromethane	85	87	50, 101, 103
Chloromethane	50	52	49
Vinyl chloride	62	64	61
Bromomethane	94	96	79
Chloroethane	64	66	49
Trichlorofluoromethane	101	103	66
1,1-Dichloroethene	96	61	98
Acrolein	56	55	58
Iodomethane	142	127	141
Carbon disulfide	76	78	
Trichlorotrifluoroethane	151	101	153
Acetone	43	58	
Methylene chloride	84	49	51, 86

Table 12 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
tert-Butyl alcohol	59	74	
trans-1,2-Dichloroethene	96	61	98
Acrylonitrile	53	52	51
Methyl <i>tert</i> butyl ether	73		
Hexane	57	43	
1,1-Dichloroethane	63	65	83
cis-1,2-Dichloroethene	96	61	98
2-Butanone	43	72**	
Tetrahydrofuran	42	71	
Chloroform	83	85	47
1,2-Dichloroethane	62	64	98
Dibromomethane	93	174	95, 172, 176
1,4-Dioxane	88	58	
Vinyl acetate	43	86	
1,1,1-Trichloroethane	97	99	117
Carbon tetrachloride	117	119	121
Benzene	78	52	77
Trichloroethene	130	95	97, 132
1,2-Dichloropropane	63	65	41
Bromodichloromethane	83	85	129
2-Chloroethyl vinyl ether	63	65	106
cis-1,3-Dichloropropene	75	77	39
trans-1,3-Dichloropropene	75	77	39
1,1,2-Trichloroethane	97	83	85, 99
Chlorodibromomethane	129	127	131
Bromoform	173	171	175, 252
1,2,3-Trichloropropane	75	110	77, 112, 97
Toluene-d ₈ (Surrogate)	98	70	100
4-Bromofluorobenzene (Surrogate)	95	174	176
Toluene	91	92	65
4-Methyl-2-pentanone	43	58	57, 100
Tetrachloroethene	164	166	131
Ethyl methacrylate	69	41	99, 86, 114
2-Hexanone	43	58	57, 100
Chlorobenzene	112	114	77
Ethylbenzene	106	91	
Xylenes	106	91	
Styrene	104	103	78, 51, 77
Dichlorobenzene (all isomers)	146	148	111
trans 1,4-Dichloro-2-butene	53	75	89, 77, 124
1,1,2,2-Tetrachloroethane	83	85	131, 133

Table 12 - Characteristic Ions

Compound	Primary*	Secondary	Tertiary
Allyl Chloride	76	41	78
Acetonitrile	40	41	
Dichlorofluoromethane	67	69	
Isopropyl ether	87	59	45
Chloroprene	53	88	90
n-Butanol	56	41	42
Propionitrile	54	52	55
Methacrylonitrile	41	67	52
Isobutanol	41	43	74
Methyl methacrylate	41	69	100
1,1,1,2-Tetrachloroethane	131	133	119
1,2-Dibromo -3-chloropropane	157	155	75
Ethyl ether	59	74	
Ethyl Acetate	43	88	61
2-Nitropropane	41	43	46
Cyclohexanone	55	42	98
Isopropylbenzene	105	120	
Cyclohexane	56	69	84
Methyl Acetate	43	74	
Methyl cyclohexane	83	55	98

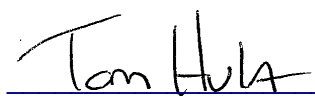
* The primary ion must be used for quantitation unless interferences are present, in which case a secondary ion may be used.

** m/z 43 may be used for quantitation of 2-Butanone, but m/z 72 must be present for positive identification.

Title: GC/MS ANALYSIS BASED ON METHODS 8270C AND 8270D

[Method: SW846 8270C and 8270D]

Approvals (Signature/Date):


Technology Specialist

10/07/10
Date


Health & Safety Coordinator

10/11/10
Date


Quality Assurance Manager

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Laboratory Director

10/07/10
Date

This SOP was previously identified as SOP NC-MS-018, Rev 1, dated 12/16/08

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1. SCOPE AND APPLICATION

- 1.1 This method is based upon SW846 8270C and 8270D, and is applicable to the determination of the concentration of semivolatile organic compounds in extracts prepared from solid and aqueous matrices. Direct injection of a sample may be used in limited applications. Refer to Tables 1 and 2 for the list of compounds applicable for this method. Note that the compounds are listed in approximate retention time order. Additional compounds may be amenable to this method. If non-standard analytes are required, they must be validated by the procedures described in Section 13 before sample analysis.
- 1.2 The following compounds may require special treatment when being determined by this method:
- Benzidine can be subject to oxidative losses during solvent concentration and exhibits poor chromatography. Neutral extraction should be performed if this compound is expected.
 - Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
 - N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be distinguished from diphenylamine.
 - Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 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.
 - Hexachlorophene is not amenable to analysis by this method.
 - 3-Methylphenol cannot be separated from 4-methylphenol by the conditions specified in this method.
- 1.3 The standard reporting limit of this method for determining an individual compound is approximately 0.33 mg/kg (wet weight) for soil/sediment samples, 1 - 200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for groundwater samples. Some compounds have higher reporting limits. Refer to Tables 1 and 2 for specific reporting limits. Reporting limits will be proportionately higher for sample extracts that require dilution.

2. SUMMARY OF METHOD

- 2.1 Aqueous samples are extracted with methylene chloride using a separatory funnel and/or a continuous extractor. Solid samples are extracted with methylene chloride / acetone using sonication, or soxhlet. The extract is dried, concentrated to a final volume of 2 mL for waters and soils, and analyzed by GC/MS. Extraction procedures are detailed in SOP NC-OP-032
- 2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extracted into a gas chromatograph equipped 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 a jet separator or a 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 using an appropriate calibration curve for the intended application.

3. DEFINITIONS

- 3.1 Refer to the TestAmerica North Canton Quality Assurance Manual (QAM), current version, for definitions of terms used in this document.

4. INTERFERENCES

- 4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If an interference is detected, it is necessary to determine if the source of interference is in the preparation and/or cleanup of the samples; then take corrective action to eliminate the problem.
- 4.2 The use of high purity reagents, solvents, and gases helps to minimize interference problems.
- 4.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the sample.
- 4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of solvent to check for cross contamination.
- 4.5 Phthalate contamination is commonly observed in this analysis and its occurrence must be carefully evaluated as an indicator of a contamination problem in the sample preparation step of the analysis.

5. SAFETY PRECAUTIONS

- 5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.
- 5.2 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated must be removed and discarded; other gloves must be cleaned immediately.
- 5.3 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA

include Benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and n-nitrosodimethylamine.

- 5.4 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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.5 It is recommended that analysts break up work tasks to avoid repetitive motion tasks, such as opening a large number of vials or containers in one time period.
- 5.6 Exposure to chemicals must be maintained as low as reasonably achievable. All samples with stickers that read “Caution/Use Hood!” must be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.
- 5.7 The preparation of standards and reagents must be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.8 It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents must be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.9 Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.10 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported immediately to a Laboratory Supervisor and the EH&S Coordinator.

6. EQUIPMENT AND SUPPLIES

- 6.1 Gas Chromatograph/Mass Spectrometer System: An analytical system complete with a

temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column must be directly coupled to the source.

- 6.2 Column: 20m x 0.18mm ID, 0.36 μ m film thickness silicon-coated fused-silica capillary column (J & W Scientific DB-5.625 or equivalent). Alternate columns are acceptable if they provide acceptable performance.
- 6.3 Mass Spectrometer: Capable of scanning from 35 to 500 AMU every one second 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 all of the criteria in Table 4 when the GC/MS tuning standard is injected through the GC.
- 6.4 GC/MS Interface: Any GC-to-MS interface that gives acceptable calibration points and achieves acceptable tuning performance criteria may be used.
- 6.5 Data System: A computer system must be 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 the 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. The most recent version of the EPA/NIH Mass Spectral Library is recommended.
- 6.6 Syringe: 5 μ L Hamilton Laboratory grade syringes or equivalent.
- 6.7 Carrier gas: Ultra high purity helium.
- 6.8 Autosampler vials, inserts, and caps

7. REAGENTS AND STANDARDS

- 7.1 A minimum five-point calibration curve is prepared. The standard preparation information is detailed in the Standard Logbook. If a quadratic regression is used, six points must be analyzed for the calibration curve. The low point must be at or below the reporting limit. Refer to Table 10 for typical calibration levels for all analytes. Other calibration levels may be used, depending on instrument capability, but the low standard must support the reporting limit and the high standard defines the range of the calibration. For Ohio VAP work, the low standard must be at, or below, the reporting limit.
- 7.2 An Internal Standard solution is prepared by diluting a purchased standard. The standard preparation information is detailed in the Standard Logbook. Compounds in the I.S. Mix are acenaphthene-d10, chrysene-d12, 1,4-dichlorobenzene-d4, naphthalene-d8, perylene-d12, and phenanthrene-d10.

- 7.3 Surrogate Standard Spiking Solution: Prepare as indicated in the preparative methods. Preparation information is detailed in the Standard Logbook for the Organic Prep group. See appropriate preparation SOP. Surrogate compounds and levels are listed in Table 9.
- 7.4 GC/MS Tuning Standard: A methylene chloride solution containing decafluorotriphenylphosphine (DFTPP) is prepared. The standard preparation information is detailed in the Standard Logbook. Pentachlorophenol, benzidine, and DDT, must also be included in the Tuning Standard. All components are at 25 ug/mL.
- 7.5 The standards listed in Sections 7.1 to 7.4 must be refrigerated at $\leq 6^{\circ}\text{C}$ when not in use. Refrigeration at -10°C to -20°C may be used if it can be demonstrated that analytes do not fall out of solution at this temperature. The standards must be replaced at least once a year. Additional information can be found in SOP NC-QA-017.

8. SAMPLE PRESERVATION AND STORAGE

- 8.1 Sample extracts are stored at $4 \pm 2^{\circ}\text{C}$. Samples and extracts must be stored in suitable glass containers with Teflon®-lined caps. (Extracts will be stored for 30 days after invoicing.)
- 8.2 Water samples are extracted within seven days of sampling, and the extracts are analyzed within 40 days of extraction. Solids, sludges, and organic liquids are extracted within 14 days of sampling and the extracts are analyzed within 40 days of extraction.

9. QUALITY CONTROL

- 9.1 Initial Demonstration of Capability
- 9.1.1 For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.
- 9.1.2 For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration. For DoD projects, the initial demonstration must include an MDL study analysis of the LCS replicates and a minimum of five-point calibration.
- 9.2 Control Limits
- 9.2.1 In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined periodically. Control limits are established by the laboratory as described in SOP NC-QA-018. Control limits are easily accessible via LIMs (QC Browser program).
- 9.2.2 If samples are diluted, the surrogate and matrix spike recoveries must be reported with a DIL flag. For DoD projects, all surrogates must be within control limits.

9.2.3 All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into LIMS (when available) or other database so that accurate historical control limits can be generated.

9.2.4 Refer to the QC Program document (QA-003) for further details of control limits.

9.3 Batch - The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Batches are defined at the sample preparation stage. Batches must be kept together through the whole analytical process to the extent possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the TestAmerica North Canton QC Program document (QA-003) for further details of the batch definition.

9.4 Method Blank

9.4.1 A method blank is prepared and analyzed with each batch of samples. The method blank consists of reagent water for aqueous samples and sodium sulfate for soil samples (refer to SOP NC-OP-032 for details). Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common lab contaminants, see below). Any blank contamination above the reporting limit must be less than 1/10 of the measured concentration of any sample in the associated preparation batch. Refer to SOP NC-QA-016 for DoD requirements.

9.4.1.1 If the analyte is a common laboratory contaminant (phthalate esters), the data may be reported with qualifiers if the concentration of the analyte is less than five times the RL. Such action must be taken in consultation with the client.

9.4.1.2 Re-analysis of any samples with reportable concentrations of analytes found in the method blank is required unless other actions are agreed with the client.

9.4.1.3 If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client. NOTE: For Ohio VAP work, there can be no target analyte greater than the RL in the method blank. All samples associated with an unacceptable blank must be re-extracted and re-analyzed. The exceptions are as follows: (a) insufficient sample for re-extraction/redigestion, (b) expired holding times, or (c) the analytes detected in the Method Blank are non-detect in the associated samples.

9.4.2 The method blank must have acceptable surrogate recoveries. If surrogate recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination. If surrogate recoveries are low and there are reportable analytes in the associated samples, re-extraction of the blank and affected samples will normally be required. Consultation with the client must

take place. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted if sufficient volume of sample remains.

9.4.3 If re-analysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B", and appropriate comments must be made in a narrative to provide further documentation.

9.4.4 Refer to the TestAmerica North Canton QC Program document (QA-003) for further details of the corrective actions.

9.5 Laboratory Control Sample (LCS)

9.5.1 A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. All control analytes must be within established control limits. The LCS is spiked with the compounds listed in Table 6 unless specified by a client or agency.

9.5.2 If any control analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur. All non-controlling compounds must attain a recovery of 10% or greater if the compound is on the client's list. Corrective action may include re-extraction and re-analysis of the batch. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted if sufficient volume of sample remains.

9.5.2.1 If the batch is not re-extracted and re-analyzed, the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of acceptable reasons for not re-analyzing might be that the matrix spike and matrix spike duplicate are acceptable, and sample surrogate recoveries are good, demonstrating that the problem was confined to the LCS).

9.5.2.2 If re-extraction and re-analysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.5.2.3 The LCS must have acceptable surrogate recoveries. If surrogate recoveries are low, re-extraction of the LCS and affected samples will normally be required. Consultation with the client should take place. For Ohio VAP samples, all analytes must meet criteria or the samples must be re-extracted. The exceptions are as follows: (a) insufficient sample for re-extraction/re-digestion, (b) expired holding times, or (c) the LCS is biased high and the samples are non-detect for those analytes.

9.5.3 Ongoing monitoring of the LCS over time provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.6.1 A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every

batch of samples. The MS/MSD is spiked with the same subset of analytes as the LCS (See Table 6). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically-generated limits.

9.6.1.1 If the recovery for any component is outside QC limits for both the matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action must include re-preparation and re-analysis of the batch.

9.6.1.2 If an MS/MSD is not possible due to limited sample, then an LCS duplicate must be analyzed. RPD of the LCS and LCSD are compared to in-house limits.

9.6.1.3 The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7 Surrogates

9.7.1 Every sample, blank, and QC sample is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. The compounds routinely included in the surrogate spiking solution, along with recommended standard concentrations, are listed in Table 9.

9.7.2 If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

9.7.2.1 Check all calculations for error.

9.7.2.2 Ensure that instrument performance is acceptable.

9.7.2.3 Recalculate the data and/or re-analyze the extract if either of the above checks reveal a problem.

9.7.2.3.1 It is only necessary to reprepare / re-analyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

Note: If all associated QC meets criteria (blank, LCS/LCSD), up to one surrogate per fraction may be outside of acceptance criteria, as long as the recovery is greater than 10%. **Note:** For Ohio VAP and DoD samples, all surrogates must be within acceptance criteria. The exceptions for Ohio VAP are as follows: (a) insufficient sample for re-extraction, or (b) the surrogates are biased high and the samples are non-detect.

9.7.3 If the sample with surrogate recoveries outside the recovery limits was a sample used for an MS/MSD and the surrogate recoveries in the MS/MSD are also outside of the control limits, then the sample, the MS, and the MSD do not require re-analysis as this phenomenon would indicate a possible matrix problem.

9.7.4 If the sample is re-analyzed and the surrogate recoveries in the re-analysis are acceptable, then the problem was within the analyst's control and only the re-analyzed data must be reported (unless the re-analysis was outside holding times, in which case, reporting both sets of results may be appropriate).

9.7.5 If the re-analysis does confirm the original results, the original analysis is reported and the data flagged as estimated due to matrix effect.

9.8 Nonconformance and Corrective Action

9.8.1 Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action approved by the facility QA Manager.

10. CALIBRATION AND STANDARDIZATION

10.1 Summary

10.1.1 The instrument is tuned for DFTPP, calibrated initially with a minimum five-point calibration curve, and verified each 12-hour shift with one or more continuing calibration standard(s). Recommended instrument conditions are listed in Table 3.

10.1.2 For DoD work, refer to SOP NC-QA-016 for specific details.

10.2 All standards and extracts are allowed to warm to room temperature before injecting.

10.3 Instrument Tuning

10.3.1 At the beginning of every 12-hour shift when analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria (Table 4) is achieved for DFTPP (decafluorotriphenylphosphine).

10.3.2 Inject the GC/MS tuning standard (Section 7.4) into the GC/MS system. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 4 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed.

10.3.3 The GC/MS tuning standard must also be used to evaluate the inertness of the chromatographic system. The tailing factor for benzidine must be less than 3.0. The tailing factor for pentachlorophenol must be less than 5. For Method 8270D, benzidine and pentachlorochlorophenol should be present at their normal responses, and should not

exceed a tailing factor of 2. DDT must be included in the tuning standard, and its breakdown must be < 20%. Refer to Section 12 for the appropriate calculations.

10.4 Initial Calibration

- 10.4.1 Internal Standard Calibration Procedure. Internal standards are listed in Table 5. Use the base peak m/z as the primary m/z for quantitation of the standards. If interferences are noted, use one of the next two most intense masses for quantitation.
- 10.4.2 Compounds should be assigned to the IS with the closest retention time. Refer to Table 11 for internal standard corresponding analytes.
- 10.4.3 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest. Six standards must be used for a quadratic least squares calibration. It may also be useful to analyze six calibration levels and use the lower five for most analytes and the upper five for analytes that have poor response. Add the internal standard mixture to result in 2 ng on column. (For example, 5 uL of 80ppm IS mix is added to 100 uL of extract. This results in 4 ng; but only 0.5 uL is injected, resulting in a final on column amount of 2 ng.). The concentration ranges of all analytes are listed in Table 10. For Ohio VAP work, the low standard must be at or below the reporting limit.
- 10.4.4 Analyze each calibration standard and tabulate the area of the primary characteristic m/z against concentration for each compound and internal standard. Table 5 lists the analytes and characteristic ions analyzed in the laboratory. Calculate response factors (RF), average response factors, and the percent RSD of the response factors for each compound using the equations in Section 12. For Method 8270C, verify that the SPCC and CCC criteria in Sections 10.4.5 and 10.4.7 are met. **No sample analysis must be performed unless these criteria are met.**
- 10.4.5 System Performance Check Compounds (SPCCs) (Method 8270C). The minimum average RF for semivolatile SPCCs is 0.050. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Some possible problems are 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 analysis begins.
- SPCC Compounds:
- N-nitroso-di-n-propylamine
 - Hexachlorocyclopentadiene
 - 2,4-Dinitrophenol
 - 4-Nitrophenol

10.4.6 Initial Calibration Criteria for Method 8270D

10.4.6.1 The RSD should be less than 20% for each analyte. For analytes that fail, use linear or quadratic curve with 0.99 correlation coefficient.

NOTE: If compliance with Method 8270C is required, the RSD limit is 15%.

10.4.6.2 No more than 10% of compounds can fail the 20%/0.99 correlation requirement.

10.4.6.3 If more than 10% of analytes fail both 20% RSD and 0.99 correlation, then recalibration is necessary.

10.4.6.4 Any individual analyte that fails both 20% RSD and 0.99 correlation must have any positive result flagged as estimated (or can be noted in the narrative).

10.4.6.5 For any analyte non-detect associated with a calibration that fails the 20% RSD/0.99 correlation/minimum response factor criteria, there must be a demonstration of adequate sensitivity at the quantitation limit.

10.4.6.6 Minimum response factor should be met, especially for the low level standard.

10.4.6.7 Any individual analyte that fails the minimum response factor set in the SOP must have a demonstration of sensitivity in the analytical batch to report non-detects. The demonstration of sensitivity is analysis of a low level CCV (at or below the reporting limit). The criterion for a passing LLCCV is detection only, and a passing LLCCV allows non-detects to be reported without flagging. The low level CCV would normally be analyzed immediately after the mid-level CCV. In general, Table 4 in the method should be used as guidance in setting minimum response factors in the SOP; but the RFs may be modified if appropriate (for example, if especially low-level analysis is performed).

10.4.6.8 For Method 8270D, the minimum response factors are listed in Table 12.

10.4.7 Calibration Check Compounds (CCCs) (Method 8270C). The %RSD of the response factors for each CCC in the initial calibration must be less than 30% for the initial calibration to be considered valid. This criterion must be met before sample analysis begins. Problems similar to those listed under SPCCs could affect this criterion.

10.4.7.1 If none of the CCCs are required analytes, project-specific calibration specifications must be agreed with the client.

10.4.7.2 CCC Compounds

Phenol

Acenaphthene
1,4-Dichlorobenzene
N-nitrosodiphenylamine
2-Nitrophenol
Pentachlorophenol
2,4-Dichlorophenol
Fluoranthene
Hexachlorobutadiene
Di-n-octylphthalate
4-Chloro-3-methylphenol
Benzo(a)pyrene
2,4,6-Trichlorophenol

10.4.7.3 Continuing Calibration Criteria for Method 8270D

10.4.7.3.1 At least 80% of analytes must have a %D less than or equal to 20%.

10.4.7.3.2 Minimum response factors must be evaluated.

10.4.8 If the software in use is capable of routinely reporting curve coefficients for data validation purposes, and the necessary calibration reports can be generated, then the analyst must evaluate analytes with %RSD > 15% for calibration on a curve. If it appears that substantially better accuracy would be obtained using quantitation from a curve, then the appropriate curve with no forced intercept must be used for quantitation.

10.4.8.1 If an analyte in the initial calibration is > 15%, then calibration on a curve must be used. Quadratic curve fits must be used if the compound has historically exhibited a nonlinear response. The analyst must consider instrument maintenance to improve the linearity of response. Use of $1/\text{Concentration}^2$ weighting is recommended to improve the accuracy of quantitation at the low end of the curve. If Relative Standard Error (RSE) is used to evaluate the curve, it must be better than 15%. If the % RSD is >15%, the analyst may drop the low or high points in the ICAL, as long as a minimum of five points are maintained and the quantitation range is adjusted accordingly. If the % RSD is still >15%, a quadratic or linear curve must be used. The coefficient of determination (r^2) must be ≥ 0.990 . If the coefficient of determination is < 0.990, then any hits for these compounds must be flagged as estimated. If a curve is not linear for any compound that is found in a sample, the result must be flagged as estimated. Linear is defined as <15% RSD or a coefficient of determination of 0.990.

Note: For Method 8270D, analytes using the linear calibration fit should have the read back concentration of the low level standard evaluated. The read back concentration should be within 30% of the true value. Any sample detects for analytes that fail the read back criterion and are using a linear calibration must be flagged as estimated, or described in the narrative.

Note: For Ohio VAP work, the low standard must be at or below the reporting limit.

Note: Several components do not respond well by this method (poor linearity). These compounds are indene, acrylamide, 4-Nitroquinoline-1-oxide, famphur, benzenethiol, kepone, and 2,4-toluenediamine. If these compounds are requested by a client and hits are found, alternate standards or methods will be needed for more accurate quantitation. Sensitivity as demonstrated by the low standard is sufficient to substantiate a non-detect.

10.4.8.2 If time remains in the 12-hour period initiated by the DFTPP injection before the initial calibration, samples must be analyzed. Otherwise, proceed to continuing calibration.

10.4.8.3 Quantitation is performed using the calibration curve or average response factor from the initial curve.

10.5 Initial Calibration Verification (ICV)

10.5.1 Calibration accuracy is verified by analyzing a second source standard (ICV) immediately after the initial calibration. The recovery CCC compounds must be $\leq 20\%$. The recovery for non-CCC compounds must be $\leq 50\%$ with an allowance of up to six compounds $>50\%$.

10.5.2 For Method 8270D, the suggested acceptance limit is 70-130% for all analytes.

10.6 Continuing Calibration

10.6.1 At the start of each 12-hour period, analyze a GC/MS tuning standard. The injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 4.

10.6.2 Following a successful DFTPP analysis the continuing calibration standard(s) are analyzed. The standards must contain all semivolatile analytes, including all required surrogates. A mid-level calibration standard is used for the continuing calibration.

10.6.3 For Method 8270C, the following criteria must be met for the continuing calibration to be acceptable:

- The SPCC compounds must have a response factor of ≥ 0.05 .
- The percent difference or drift of the CCC compounds from the initial calibration must be $\leq 20\%$ (see Section 12 for calculations). In addition, the percent difference or drift of all analytes must be $\leq 50\%$, with allowance for up to four compounds to be greater than 50%.

- The internal standard response must be within 50-200% of the response in the mid level of the initial calibration.
- The internal standard retention times must be within 30 seconds of the retention times in the mid-level of the initial calibration.

Note: There is no internal standard criteria for samples. Criteria is only for continuing and initial calibrations.

Note: Ohio VAP requires that any sample with internal standard outliers be re-analyzed undiluted unless a matrix effect is observed. If there is no matrix interference, the sample must be re-analyzed at the original dilution. If the internal standard is within criteria, report the second analysis. If the internal standard is still outside of criteria, the sample must be diluted until the internal standard meets criteria. Multiple runs may be required. The criteria for acceptance is between 50% and 200% of the same internal standard in continuing calibration.

- 10.6.3.1. If none of the CCCs are required analytes, project specific calibration specifications must be agreed with the client.
- 10.6.3.2. For Method 8270D, any sample non-detects for an analyte that fails the SOP criteria low, must have a low level CCV (CCV at the RL) in the batch as a sensitivity demonstration. The criterion for a passing LLCCV is detection only, and a passing LLCCV allows non-detect samples to be reported without flagging.
- 10.6.4. Once the above criteria have been met, sample analysis will begin. Initial calibration average RFs (or the calibration curve) will be used for sample quantitation, not the continuing calibration RFs. Analysis will proceed until 12 hours from the injection of the DFTPP have passed. (A sample *injected* less than 12 hours after the DFTPP is acceptable.)

11. PROCEDURE

11.1 Sample Preparation

- 11.1.1 Samples are prepared following SOP NC-OP-032.
- 11.1.2 For DoD work, refer to SOP NC-QA-016 for specific details.

11.2 Sample Analysis Procedure

- 11.2.1 Calibrate the instrument as described in Section 10. Depending on the target compounds required by the client, it may be necessary to use more than one calibration standard.

- 11.2.2 Analyze all samples using the same instrument conditions as the preceding continuing calibration standard.
- 11.2.3 Add internal standard to the extract to result in 2 ng injected on column. Mix thoroughly before injection into the instrument.
- 11.2.4 Inject the sample extract into the GC/MS system using the same injection technique as used for the standards.
- 11.2.5 The data system will determine the concentration of each analyte in the extract using calculations equivalent to those in Section 12. Quantitation is based on the initial calibration, not the continuing calibration.
- 11.2.6 Identified compounds are reviewed for proper integration. Manual integrations are performed if necessary and are documented by the analyst or automatically by the data system. Chromatograms before and after manual integration are required by many programs. Additional information on manual integration can be found in SOP CA-Q-S-002.
- 11.2.7 Target compounds identified by the data system are evaluated using the criteria listed in Section 12.1.
- 11.2.8 Library searches of peaks present in the chromatogram that are not target compounds (Tentatively Identified Compounds, TIC) must be performed if required by the client. They are evaluated using the criteria in Section 12.3.

11.3 Dilutions

- 11.3.1 If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution must be in the upper half of the calibration range. Samples must be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be re-analyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.
- 11.3.2 Guidance for Dilutions Due to Matrix
 - 11.3.2.1 If the sample is initially run at a dilution and the baseline rise is less than the height of the internal standards, or if individual non-target peaks are less than two times the height of the internal standards, the sample should be re-analyzed at a more concentrated dilution. This requirement is approximate and subject to analyst judgement. For example, samples containing organic acids must be analyzed at a higher dilution to avoid destroying the column.

11.3.3 Reporting Dilutions

11.3.3.1 The most concentrated dilution with target compounds within the calibration range will be reported. Other dilutions will only be reported at client request.

11.4 Perform all qualitative and quantitative measurements. When the extracts are not being used for analyses, refrigerate them at $4 \pm 2^{\circ}\text{C}$ protected from light in screw cap vials equipped with unpierced Teflon®-lined septa.

11.5 Retention Time Criteria for Samples

11.5.1 If the retention time for any internal standard changes by more than 0.5 minutes from the last continuing calibration standard, the chromatographic system must be inspected for malfunctions and corrected. Re-analysis of samples analyzed while the system was malfunctioning is required.

11.5.2 If the retention time of any internal standard in any sample varies by more than 0.1 minute from the preceding continuing calibration standard, the data must be carefully evaluated to ensure no analytes have shifted outside their retention time windows.

11.6 Procedural Variations

11.6.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. The Nonconformance Memo must be filed in the project file. Any unauthorized deviations from this procedure must also be documented as a non-conformance with a cause and corrective action described.

11.7 Troubleshooting Guide

11.7.1 Daily Instrument Maintenance

11.7.1.1 In addition to the checks listed in the instrument maintenance schedule in the TestAmerica North Canton Quality Assurance Manual (QAM), current version, the following daily maintenance must be performed.

11.7.1.1.1 Clip column as necessary.

11.7.1.1.2 Install new or cleaned injection port liner as necessary.

11.7.1.1.3 Install new septum as necessary.

11.7.1.1.4 Perform autotune.

11.7.2 Major Maintenance

- 11.7.2.1 A new initial calibration is necessary following major maintenance. Major maintenance includes changing the column, cleaning the source, and replacing the multiplier. Refer to the manufacturer's manual for specific guidance.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Qualitative Identification

- 12.1.1 An analyte is identified by retention time and by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference may be obtained on the user's GC/MS by analysis of the calibration standards or from the NBS library. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC retention time as the standard component; and (2) correspondence of the sample component and the standard component characteristic ions. (Note: Care must be taken to ensure that spectral distortion due to co-elution is evaluated.)

- 12.1.1.1 The sample component retention time must compare to within ± 0.2 min. of the retention time of the standard component. For reference, the standard must be run within the same 12 hours as the sample.

- 12.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

- 12.1.1.3 The characteristic ions of a compound must maximize in the same scan or within one scan of each other.

- 12.1.1.4 The relative intensities of ions must agree to within $\pm 30\%$ between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%.)

- 12.1.2 If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst must report that identification and proceed with quantitation.

12.2 Mass chromatogram searches

- 12.2.1 Certain compounds are unstable in the calibration standard and cannot be calibrated in the normal way. In particular, the compound hexachlorophene (CAS 70-30-4) falls into this category, and is required for Appendix IX analysis. For this analyte, a mass chromatogram search is made.

- 12.2.1.1 Hexachlorophene

- 12.2.1.1.1 Display the mass chromatograms for mass 196 and mass 198 for the region of the chromatogram from at least 2 minutes before chrysene-d12 to at least 4 minutes after chrysene-d12. If peaks for both ions coincide, then the analyst evaluates the spectrum for the presence of hexachlorophene. No quantitation is possible.
- 12.3 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 must be determined by the type of analyses being conducted or by client request. Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:
- 12.3.1 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) must be present in the sample spectrum.
- 12.3.2 The relative intensities of the major ions must agree within $\pm 20\%$. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%.)
- 12.3.3 Molecular ions present in the reference spectrum must be present in the sample spectrum.
- 12.3.4 Ions present in the sample spectrum, but not in the reference spectrum, must be reviewed for possible background contamination or presence of co-eluting compounds.
- 12.3.5 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 co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.
- 12.3.6 Automatic background subtraction can severely distort spectra from samples with unresolved hydrocarbons.
- 12.3.7 Note: For water samples, the TIC searches begin with compounds eluting after the first surrogate (2-Fluorophenol). For solid samples, the TIC searches begin with compounds eluting after the Aldol Condensation Product. Any compounds eluting before these analytes are considered volatile analytes are reported in the volatile analysis. A possible exception to this general rule would be if an early eluting compound were the reason for a sample dilution.
- 12.3.8 If a client requests 10 TICs, the laboratory supplies a minimum of 10. For a request of 20 TICs, the laboratory would supply a minimum of 20--assuming that number of compounds were available.

- 12.4 Anyone evaluating data is trained to know how to handle isomers with identical mass spectra and close elution times. These include:

Dichlorobenzenes
Methylphenols
Trichlorophenols
Phenanthrene, anthracene
Fluoranthene, pyrene
Benzo(b) and (k)fluoranthene
Chrysene, benzo(a)anthracene

Extra precautions concerning these compounds are to more closely scrutinize retention time vs. the calibration standard and also to check that all isomers have distinct retention times.

A second category of problem compounds would be the poor responders or compounds that chromatograph poorly. Included in this category would be:

Benzoic acid
Chloroanilines
Nitroanilines
2,4-Dinitrophenol
4-Nitrophenol
Pentachlorophenol
3,3'-Dichlorobenzidine
Benzyl alcohol
4,6-Dinitro-2-methylphenol

Manually checking the integrations would be appropriate for these compounds.

12.5 Calculations

12.5.1 Percent Relative Standard Deviation for Initial Calibration

$$\%RSD = \frac{SD}{RF} \times 100$$

RF = Mean of RFs from initial calibration for a compound

SD = Standard deviation of RFs from initial calibration for a compound,

$$= \sqrt{\sum_{i=1}^N \frac{(RF_i - \overline{RF})^2}{N - 1}}$$

RF_i = RF for each of the calibration levels

N = Number of RF values

12.5.2 Continuing calibration percent drift

$$\%Drift = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100\%$$

C_{actual} = Known concentration in standard

C_{found} = Measured concentration using selected quantitation method

12.5.3 Concentration in the extract

The concentration of each identified analyte and surrogate in the extract is calculated from the linear or quadratic curve fitted to the initial calibration points, or from the average RF of the initial calibration.

12.5.3.1 Average Response Factor

If the average of all the %RSDs of the response factors in the initial calibration is $\leq 15\%$, the average response factor from the initial calibration may be used for quantitation.

$$C_{ex} = \frac{R_x C_{is}}{R_{is} RF}$$

12.5.3.2 Linear fit

$$C_{ex} = A + B \frac{(R_x C_{is})}{R_{is}}$$

Where:

- C_{ex} = Concentration in extract, $\mu\text{g/mL}$
- R_x = Response for analyte
- C_{is} = Concentration of internal standard
- A = Intercept
- B = Slope

12.5.3.3 Quadratic fit

$$C_{ex} = A + B\left(\frac{R_x C_{is}}{R_{is}}\right) + C\left(\frac{R_x C_{is}^2}{R_{is}}\right)$$

Where: C = Curvature

12.5.4 The concentration in the sample is then calculated.

12.5.4.1 Aqueous Calculation

$$\text{Concentration, } \mu\text{g} / \text{L} = \frac{C_{ex} V_t}{V_o}$$

Where: V_t = Volume of total extract, μL , taking into account dilutions (i.e., a 1-to-10 dilution of a 1 mL extract will mean $V_t = 10,000 \mu\text{L}$. If half the base/neutral extract and half the acid extract are combined, $V_t = 2,000$.)

V_o = Volume of water extracted (mL)

12.5.5 Sediment/Soil, Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis)

$$\text{Concentration, } \mu\text{g} / \text{kg} = \frac{C_{ex} V_t}{W_s D}$$

Where: W_s = Weight of sample extracted or diluted in grams
D = (100 - % moisture in sample)/100, for a dry weight basis or one for a wet weight basis

12.6 MS/MSD percent recovery calculation.

$$\text{Matrix Spike Recovery} = \frac{S_{SR} - S_R}{S_A} \times 100\%$$

Where: S_{SR} = Spike sample result
 S_R = Sample result
 S_A = Concentration equivalent of spike added

12.7 Relative % Difference calculation for the MS/MSD

$$RPD = \frac{MS_R - MSD_R}{1 / 2 (MS_R + MSD_R)} \times 100$$

Where: RPD = Relative percent difference
 MS_R = Matrix spike result
 MSD_R = Matrix spike duplicate result

12.8 Relative response factor calculation

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where: A_x = Area of the characteristic ion for the compound being measured
 A_{is} = Area of the characteristic ion for the specific internal standard
 C_x = Concentration of the compound being measured (µg/L)
 C_{is} = Concentration of the specific internal standard (µg/L)

12.9 Calculation of TICs: The calculation of TICs (tentatively identified compounds) is identical to the above calculations with the following exceptions:

A_x = Area of the total ion chromatogram for the compound being measured
 A_{is} = Area of the total ion chromatogram for the nearest internal standard without interference
 RF = 1

12.10 Percent DDT breakdown

$$\% \text{ DDT breakdown} = \frac{\text{DDEarea} + \text{DDDarea}}{\text{DDTarea} + \text{DDEarea} + \text{DDarea}}$$

The total ion current areas are used for this calculation

12.11 Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002

13. METHOD PERFORMANCE

13.1 Method Detection Limit

13.1.1 Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in Policy CA-Q-S-006 and SOP NC-QA-021.

13.2 Initial Demonstration

13.2.1 Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of Laboratory Control Samples (LCS) containing all of the standard analytes for the method. For some tests, it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1.1 Four aliquots of the LCS are analyzed using the same procedures used to analyze samples, including sample preparation.

13.2.1.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

13.2.1.3 If any analyte does not meet the LCS acceptance criteria the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3 Training Qualification

13.3.1 The Group/Team Leader has the responsibility to ensure this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13.3.2 Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1 This section is not applicable to this procedure.

15. WASTE MANAGEMENT

15.1 All waste will be disposed of in accordance with Federal, State and Local laws and 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 Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2 Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

15.3 Waste Streams Produced by the Method

- 15.3.1 Vials containing sample extracts. These vials are placed in the vial waste located in the GC/MS laboratory.

16. REFERENCES

16.1 References

- 16.1.1 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update III October 1994, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique, Method 8270C
- 16.1.2 J. W. Eichelberger, L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography/Mass Spectrometry," Analytical Chemistry, 47, 995 (1975)
- 16.1.3 [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version
- 16.1.4 TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version
- 16.1.5 [Corporate Quality Management Plan \(CQMP\)](#), current version
- 16.1.6 Revision History

Historical File:	Revision 2.1: 01/25/99	Revision 0: 05/28/08 (NC-MS-018)
(formerly CORP-MS-0001NC)	Revision 2.2: 03/27/00	Revision 1: 12/16/08
	Revision 2.3: 02/15/01	
	Revision 2.4: 05/29/01	
	Revision 2.5: 04/25/02	
	Revision 2.6: 08/15/02	
	Revision 2.7: 11/12/02	
	Revision 2.8: 01/23/03	
	Revision 2.9: 06/18/03	
	Revision 2.10: 02/24/04	
	Revision 2.11: 02/03/06	
	Revision 2.12: 03/01/07	

16.2 Associated SOPs and policies, current version

- 16.2.1 QA Policy, [QA-003](#)
- 16.2.2 Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)
- 16.2.3 Method Detection Limits and Instrument Detection Limits, [NC-QA-021](#) and [CA-Q-S-006](#)

16.2.4 Supplemental Practices for DoD Project Work, [NC-QA-016](#)

16.2.5 Standard and Reagents, [NC-QA-017](#)

16.2.6 Acceptable Manual Integration Practices, [CA-Q-S-002](#)

16.2.7 Calibration Curves (General), [CA-Q-S-005](#)

16.2.8 Section of Calibration Points, [CA-T-P-002](#)

17. MISCELLANEOUS

17.1 Modifications from Reference Method

17.1.1 A retention time window of 0.2 minutes is used for all components, since some data systems do not have the capability of using the relative retention time units specified in the reference method.

17.1.2 The quantitation and qualifier ions from compounds have been changed from those recommended in SW-846 in order to improve the reliability of qualitative identification.

17.2 Tables

TABLE 1: TestAmerica North Canton Standard Reporting Limits

Analytes	CAS Number	Water µg/L	Soil µg/kg	Low Level Water, µg/L	Low Level Soil, µg/kg	TCLP mg/L
1,1-Biphenyl	92-52-4	10	330	1	50	
1,2,4-Trichlorobenzene	120-82-1	10	330	1	50	
1,2-Dichlorobenzene	95-50-1	10	330	1	50	
1,3-Dichlorobenzene	541-73-1	10	330	1	50	
1,4-Dichlorobenzene	106-46-7	10	330	1	50	0.004
1-Methyl Naphthalene	90-12-0	10	330	0.2	6.67	
2,2'-oxybis(1-chloropropane) ¹	108-60-1	10	330	1	100	
2,4,5-Trichlorophenol	95-95-4	10	330	5	150	0.02
2,4,6-Trichlorophenol	88-06-2	10	330	5	150	0.02
2,4-Dichlorophenol	120-83-2	10	330	2	150	
2,4-Dimethylphenol	105-67-9	10	330	2	150	
2,4-Dinitrophenol	51-28-5	50	1600	5	330	
2,4-Dinitrotoluene	121-14-2	10	330	5	200	0.02
2,6-Dinitrotoluene	606-20-2	10	330	5	200	
2-Chloronaphthalene	91-58-7	10	330	1	50	
2-Chlorophenol	95-57-8	10	330	1	50	
2-Methylnaphthalene	91-57-6	10	330	0.2	6.67	
2-Methylphenol	95-48-7	10	330	1	200	
2-Nitroaniline	88-74-4	50	1600	2	200	
2-Nitrophenol	88-75-5	10	330	2	50	
3,3'-Dichlorobenzidine	91-94-1	50	1600	5	100	
3-Nitroaniline	99-09-2	50	1600	2	200	
4,6-Dinitro-2-methylphenol	534-52-1	50	1600	5	150	
4-Bromophenyl phenyl ether	101-55-3	10	330	2	50	
4-Chloro-3-methylphenol	59-50-7	10	330	2	150	
4-Chloroaniline	106-47-8	10	330	2	150	
4-Chlorophenyl phenyl ether	7005-72-3	10	330	2	50	
4-Methylphenol	106-44-5	10	330	1	200	
4-Nitroaniline	100-01-6	50	1600	2	200	
4-Nitrophenol	100-02-7	50	1600	5	330	
Acenaphthene	83-32-9	10	330	0.2	6.67	
Acenaphthylene	208-96-8	10	330	0.2	6.67	
Aniline	62-53-3	10	330	5	330	
Anthracene	120-12-7	10	330	0.2	6.67	
Atrazine	1912-24-9	10	330	1	200	
Azobenzene	103-33-3	10	330	10	330	
Benzaldehyde	100-52-7	10	330	1	100	
Benzenethiol	108-98-5	10	330	10	330	
Benzidine	92-87-5	100	3300	5	660	
Benzo(a)anthracene	56-55-3	10	330	0.2	6.67	
Benzo(a)pyrene	50-32-8	10	330	0.2	6.67	
Benzo(b)fluoranthene	205-99-2	10	330	0.2	6.67	
Benzo(g,h,i)perylene	191-24-2	10	330	0.2	6.67	
Benzo(k)fluoranthene	207-08-9	10	330	0.2	6.67	

Analytes	CAS Number	Water $\mu\text{g/L}$	Soil $\mu\text{g/kg}$	Low Level Water, $\mu\text{g/L}$	Low Level Soil, $\mu\text{g/kg}$	TCLP mg/L
Benzoic acid	65-85-0	50	1600	25	660	
Benzyl alcohol	100-51-6	10	330	5	330	
Bis(2-chloroethoxy)methane	111-91-1	10	330	1	100	
Bis(2-chloroethyl)ether	111-44-4	10	330	1	100	
Bis(2-ethylhexyl)phthalate	117-81-7	10	330	2	50	
Butyl benzyl phthalate	85-68-7	10	330	1	50	
Caprolactam	105-60-2	10	330	5	330	
Carbazole	86-74-8	10	330	1	50	
Chrysene	218-01-9	10	330	0.2	6.67	
Dibenz(a,h)anthracene	53-70-3	10	330	0.2	6.67	
Dibenzofuran	132-64-9	10	330	1	50	
Diethylphthalate	84-66-2	10	330	1	50	
Dimethyl phthalate	131-11-3	10	330	1	50	
Di-n-butyl phthalate	84-74-2	10	330	1	50	
Di-n-octylphthalate	117-84-0	10	330	1	50	
Fluoranthene	206-44-0	10	330	0.2	6.67	
Fluorene	86-73-7	10	330	0.2	6.67	
Hexachlorobenzene	118-74-1	10	330	0.2	6.67	0.02
Hexachlorobutadiene	87-68-3	10	330	1	50	0.02
Hexachlorocyclopentadiene	77-47-4	10	1600	10	330	0.05
Hexachloroethane	67-72-1	10	330	1	50	
Indene	95-13-6	10	330	5	330	
Indeno(1,2,3-cd)pyrene	193-39-5	10	330	0.2	6.67	
Isophorone	78-59-1	10	330	1	50	
Naphthalene	91-20-3	10	330	0.2	6.67	
Nitrobenzene	98-95-3	10	330	1	100	0.004
N-nitrosodimethylamine	62-75-9	10	330	1	100	
N-Nitroso-di-n-propylamine	621-64-7	10	330	1	50	
N-Nitrosodiphenylamine	86-30-6	10	330	1	50	
Pentachlorophenol	87-86-5	10	330	5	150	0.04
Phenanthrene	85-01-8	10	330	0.2	6.67	
Phenol	108-95-2	10	330	1	50	
Pyrene	129-00-0	10	330	0.2	6.67	
Pyridine	110-86-1	20	660	1	100	0.02
Quinoline	91-22-5	10	330	5	330	
m-Cresol & p Cresol						0.04
o-Cresol						0.004
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330	1	100	
1,3,5-Trinitrobenzene	99-35-4	50	1600	5	1600	
1,3-Dinitrobenzene	99-65-0	10	330	2	330	
1,4-Dinitrobenzene	100-25-4	10	330	2	100	
1,4-Naphthoquinone	130-15-4	50	1600	50	330	
1-Naphthylamine	134-32-7	10	330	2	330	
2,3,4,6-Tetrachlorophenol	58-90-2	50	1600	10	100	
2,6-Dichlorophenol	87-65-0	10	330	5	150	
2-Acetylaminofluorene	53-96-3	100	3300	10	330	

Analytes	CAS Number	Water µg/L	Soil µg/kg	Low Level Water, µg/L	Low Level Soil, µg/kg	TCLP mg/L
2-Naphthylamine	91-59-8	10	330	2	200	
2-Picoline	109-06-8	20	660	5	330	
2-secbutyl-4,6-dinitrophenol (Dinoseb2)	88-85-7	20	660	2	330	
3,3'-Dimethylbenzidine	119-93-7	50	1600	5	330	
3-Methylcholanthrene	56-49-5	20	660	5	200	
3-Methylphenol	108-39-4	10	330	1	200	
4-Aminobiphenyl	92-67-1	50	1600	5	330	
4-Nitroquinoline-1-oxide	56-57-5	100	3300	5	330	
5-Nitro-o-toluidine	99-55-8	20	660	2	330	
7,12-Dimethylbenz(a)anthracene	57-97-6	20	660	2	330	
a,a-Dimethyl-phenethylamine	122-09-8	50	1600	5	660	
Acetophenone	98-86-2	10	330	1	100	
Aramite	140-57-8	20	660	5	330	
Diallate ²	2303-16-4	20	660	10	330	
Dibenz(a,j)acridine	224-42-0	20	660	5	330	
Dimethoate	60-51-5	20	660	2	330	
Disulfoton	298-04-4	50	1600	2	330	
Ethyl methanesulfonate	62-50-0	10	330	2	330	
Famphur	52-85-7	100	3300	10	3300	
Hexachloropropene	1888-71-7	100	3300	5	0.02	
Isosafrole	120-58-1	20	660	5	330	
Methapyrilene	91-80-5	50	1600	2	330	
Methyl methanesulfonate	66-27-3	10	330	2	330	
N-Nitrosodiethylamine	55-18-5	10	330	2	100	
n-Nitrosodi-n-butylamine	924-16-3	10	330	2	100	
N-Nitrosomethylethylamine	10595-95-6	10	330	2	100	
N-Nitrosomorpholine	59-89-2	10	330	2	330	
N-Nitrosopiperidine	100-75-4	10	330	2	330	
N-Nitrosopyrrolidine	930-55-2	10	330	2	50	
o,o,o-Triethyl-Phosphorothioate	126-68-1	50	1600	2	330	
o-Toluidine	95-53-4	20	660	2	330	
p-(Dimethylamino)azobenzene	60-11-7	20	660	2	330	
p-Chlorobenzilate	510-15-6	10	330	2	330	
Pentachlorobenzene	608-93-5	10	330	2	100	
Pentachloroethane	76-01-7	50	1600	20	330	
Pentachloronitrobenzene	82-68-8	50	1600	2	330	
Phenacetin	62-44-2	20	660	2	330	
Phorate	298-02-2	50	1600	2	330	
p-Phenylenediamine	106-50-3	100	3300	40	660	
Pronamide	23950-58-5	20	660	2	330	
Safrole	94-59-7	20	660	2	330	
Sulfotepp	3689-24-5	50	1600	5	330	
Thionazin	297-97-2	50	1600	2	330	
1,2,4,5-Tetrachlorobenzene	95-94-3	10	330	1	100	
1,3,5-Trinitrobenzene	99-35-4	50	1600	5	1600	
1,3-Dinitrobenzene	99-65-0	10	330	2	330	

Analytes	CAS Number	Water µg/L	Soil µg/kg	Low Level Water, µg/L	Low Level Soil, µg/kg	TCLP mg/L
1,4-Dinitrobenzene	100-25-4	10	330	2	100	

1 2,2'-oxybis(1-chloropropane) was formerly known as bis(2-chloroisopropyl)ether.

Skinner List Compound

Hexachlorophene is a required analyte for Appendix IX. This compound is not stable, and therefore not included in the calibration standard. The characteristic ions for hexachlorophene are searched for in the chromatogram (see Section 12.2.1).

Diphenylamine is a required compound for Appendix IX. N-nitrosodiphenylamine decomposes in the injection port to form diphenylamine. Therefore, these two compounds cannot be distinguished. Diphenylamine is not included in the calibration standard.

TABLE 2: TestAmerica North Canton Michigan Program¹

Semivolatile	CAS Number	Michigan Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
Acenaphthene	83-32-9	5	330
Acenaphthylene	208-96-8	5	330
Acetophenone	98-86-2	5	330
Anthracene	120-12-7	5	330
Atrazine	1912-24-9	5	330
Benzaldehyde	100-52-7	10	330
Benzo(a)anthracene	56-55-3	1	330
Benzo(a)pyrene	50-32-8	2	330
Benzo(b)fluoranthene	205-99-2	2	330
Benzo(g,h,i)perylene	191-24-2	5	330
Benzo(k)fluoranthene	207-08-9	5	330
1,1'-Biphenyl	92-52-4	10	330
4-Bromophenylphenyl ether	101-55-3	5	330
Butylbenzylphthalate	85-68-7	5	330
di-n-Butylphthalate	84-74-2	5	330
Caprolactam	105-60-2	10	330
Carbazole	86-74-8	10	330
4-Chloroaniline	106-47-8	20	1700
bis(2-Chloroethoxy)methane	111-91-1	5	330
bis(2-Chloroethyl)ether	111-44-4	4	330
bis(2-Chloroisopropyl)ether	108-60-1	5	330
4-Chloro-3-Methylphenol	59-50-7	5	330
2-Chloronaphthalene	91-58-7	5	330
2-Chlorophenol	95-57-8	5	330
4-Chlorophenyl phenyl ether	7005-72-3	5	330
Chrysene	218-01-9	5	330

		Michigan Reporting Limits	
Dibenz(a,h)anthracene	53-70-3	2	330
Dibenzofuran	132-64-9	5	330
3,3'-Dichlorobenzidine	91-94-1	4	2000
2,4-Dichlorophenol	120-83-2	10	330
Diethylphthalate	84-66-2	5	330
2-4-Dimethylphenol	105-67-9	5	330
Dimethylphthalate	131-11-3	5	330

Semivolatile	CAS Number	Michigan Reporting Limits	
		Aqueous µg/L	Low Soil/Sediment µg/kg
4,6-Dinitro-2-methylphenol	534-52-1	20	1700
2,4-Dinitrophenol	51-28-5	20	1700
2,4-Dinitrotoluene	121-14-2	5	330
2,6-Dinitrotoluene	606-20-2	5	330
bis(2-Ethylhexyl)phthalate	117-81-7	5	330
Fluoranthene	206-44-0	5	330
Fluorene	86-73-7	5	330
Hexachlorobenzene	118-74-1	5	330
Hexachlorobutadiene	87-68-3	5	330
Hexachlorocyclopentadiene	77-47-4	5	330
Hexachloroethane	67-72-1	5	330
Indeno(1,2,3-cd)pyrene	193-39-5	2	330
Isophorone	78-59-1	5	330
2-Methylnaphthalene	91-57-6	5	330
2-Methylphenol	95-48-7	5	330
4-Methylphenol	106-44-5	5	330
Naphthalene	91-20-3	5	330
2-Nitroaniline	88-74-4	20	1700
3-Nitroaniline	99-09-2	20	1700
4-Nitroaniline	100-01-6	20	1700
Nitrobenzene	95-95-3	4	330
2-Nitrophenol	88-75-5	5	330
4-Nitrophenol	100-02-7	20	1700
N-Nitroso-di-n-propylamine	621-64-7	5	330
N-Nitrosodiphenylamine (diphenylamine)	62-75-9	5	330
di-n-Octylphthalate	117-84-0	5	330
Pentachlorophenol	87-86-5	20	800
Phenanthrene	85-01-8	5	330
Phenol	108-95-2	5	330
Pyrene	129-00-0	5	330
2,4,5-Trichlorophenol	95-95-4	5	330
2,4,6-Trichlorophenol	88-06-2	4	330

¹ Reporting Limits are only for samples performed under the Michigan program.

TABLE 3: Suggested Instrument Conditions

Mass Range	35-500 amu
Scan Time	≤1 second/scan
Initial Column Temperature/Hold Time	60°C for 1 minutes
Column Temperature Program	60 - 320°C at 35°C/min for 3 min
Final Column Temperature/Hold Time	320°C (until at least one minute after benzo(g,h,i)perylene has eluted)
Injector Temperature	250 - 300°C
Transfer Line Temperature	250 - 300°C
Source Temperature	According to manufacturer's Specifications
Injector	Grob-type, split / splitless
Sample Volume	0.5 µl
Carrier Gas	Helium at 30 cm/sec

TABLE 4: DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30 – 80% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	25 - 75% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 – 9% of mass 198
275	10 – 30% of mass 198
365	> 0.75% of mass 198
441	Present, but less than mass 443
442	40 - 110% of mass 198
443	15 - 24% of mass 442

TABLE 5: Analytes in Approximate Retention Time Order and Characteristic Ions

Analyte	Primary	Secondary	Tertiary
N-nitrosodimethylamine	74	42	
Pyridine	79	52	
2-Fluorophenol (Surrogate Standard)	112	64	63
Phenol-d5 (Surrogate Standard)	99	42	71
Benzaldehyde	77	105	106
Aniline	93	66	
Phenol	94	65	66
Bis(2-chloroethyl)ether	93	63	95
2-Chlorophenol	128	64	130
1,3-Dichlorobenzene	146	148	113
1,4-Dichlorobenzene-d4 (Internal Standard)	152	150	115
1,4-Dichlorobenzene	146	148	113
Benzyl Alcohol	108	79	77
1,2-Dichlorobenzene	146	148	113
2-Methylphenol	108	107	79
2,2'-oxybis(1-chloropropane) ¹	45	77	79
4-Methylphenol	108	107	79
N-Nitroso-di-n-propylamine	70	42	101,130
Hexachloroethane	117	201	199
Nitrobenzene-d5 (Surrogate Standard)	82	128	54
Nitrobenzene	77	123	65
Isophorone	82	95	138
2-Nitrophenol	139	65	109
2,4-Dimethylphenol	107	121	122
Benzoic Acid	122	105	77
Bis(2-chloroethoxy)methane	93	95	123
2,4-Dichlorophenol	162	164	98
1,2,4-Trichlorobenzene	180	182	145
Naphthalene-d8 (Internal Standard)	136	68	54
Naphthalene	128	129	127
4-Chloroaniline	127	129	65
Hexachlorobutadiene	225	223	227
Caprolactam	113	55	56
4-Chloro-3-methylphenol	107	144	142
2-Methylnaphthalene	142	141	115
Hexachlorocyclopentadiene	237	235	272
2,4,6-Trichlorophenol	196	198	200
2,4,5-Trichlorophenol	196	198	200
1,1'-Biphenyl	154	153	76
2-Fluorobiphenyl (Surrogate Standard)	172	171	170
2-Chloronaphthalene	162	164	127
2-Nitroaniline	65	92	138
Dimethylphthalate	163	194	164
Acenaphthylene	152	151	153

TABLE 5: Analytes in Approximate Retention Time Order and Characteristic Ions

Analyte	Primary	Secondary	Tertiary
2,6-Dinitrotoluene	165	63	89

Analyte	Primary	Secondary	Tertiary
Acenaphthene-d10 (Internal Standard)	164	162	160
3-Nitroaniline	138	108	92
Acenaphthene	153	152	154
2,4-Dinitrophenol	184	63	154
Dibenzofuran	168	139	84
4-Nitrophenol	109	139	65
2,4-Dinitrotoluene	165	63	89
Diethylphthalate	149	177	150
Fluorene	166	165	167
4-Chlorophenylphenylether	204	206	141
4-Nitroaniline	138	92	108
4,6-Dinitro-2-methylphenol	198	182	77
N-Nitrosodiphenylamine	169	168	167
2,4,6-Tribromophenol (Surrogate Standard)	330	332	141
Azobenzene	77	182	105
4-Bromophenylphenylether	248	250	141
Hexachlorobenzene	284	142	249
Atrazine	200	173	215
Pentachlorophenol	266	264	268
Phenanthrene-d10 (Internal Standard)	188	94	80
Phenanthrene	178	179	176
Anthracene	178	179	176
Carbazole	167	166	139
Di-n-butylphthalate	149	150	104
Fluoranthene	202	101	100
Benzidine	184	92	185
Pyrene	202	101	100
Terphenyl-d14 (Surrogate Standard)	244	122	212
Butylbenzylphthalate	149	91	206
Benzo(a)Anthracene	228	229	226
Chrysene-d12 (Internal Standard)	240	120	236
3,3'-Dichlorobenzidine	252	254	126
Chrysene	228	226	229
Bis(2-ethylhexyl)phthalate	149	167	279
Di-n-octylphthalate	149	167	43
Benzo(b)fluoranthene	252	253	125
Benzo(k)fluoranthene	252	253	125
Benzo(a)pyrene	252	253	125
Perylene-d12 (Internal Standard)	264	260	265
Indeno(1,2,3-cd)pyrene	276	138	277
Dibenz(a,h)anthracene	278	139	279
Benzo(g,h,i)perylene	276	138	277
2-Picoline	93	66	92

Analyte	Primary	Secondary	Tertiary
N-Nitrosomethylethylamine	88	42	43
Methyl methanesulfonate	80	79	65
N-Nitrosodiethylamine	102	44	57
Ethyl methanesulfonate	79	109	97
Pentachloroethane	117	119	167
Acetophenone	105	77	120
N-Nitrosopyrrolidine	100	41	42
N-Nitrosomorpholine	116	56	86
o-Toluidine	106	107	
3-Methylphenol	108	107	77
N-Nitrosopiperidine	114	42	55
o,o,o-Triethyl-Phosphorothioate	198	121	93
a,a-Dimethyl-phenethylamine	58	91	
2,6-Dichlorophenol	162	164	63
Hexachloropropene	213	215	211
p-Phenylenediamine	108	80	
n-Nitrosodi-n-butylamine	84	57	41
Safrole	162	104	77
1,2,4,5-Tetrachlorobenzene	216	214	218
Isosafrole 1	162	104	131
Isosafrole 2	162	104	131
1,4-Dinitrobenzene	168	75	122
1,4-Naphthoquinone	158	104	102
1,3-Dinitrobenzene	168	75	76
Pentachlorobenzene	250	248	252
1-Naphthylamine	143	115	
2-Naphthylamine	143	115	
2,3,4,6-Tetrachlorophenol	232	230	131
5-Nitro-o-toluidine	152	77	106
Thionazin	97	96	143
1,3,5-Trinitrobenzene	213	75	120
Sulfotepp	97	322	202
Phorate	75	97	121
Phenacetin	108	179	109
Diallate	86	234	
Dimethoate	87	93	125
4-Aminobiphenyl	169		
Pentachloronitrobenzene	237	142	214
Pronamide	173	175	255
Disulfoton	88	97	89
2-secbutyl-4,6-dinitrophenol (Dinoseb)	211	163	147
Methyl parathion	109	125	263
4-Nitroquinoline-1-oxide	190	128	160
Famphur	218	125	93
Methapyrilene	97	58	
Aramite 1	185	319	
Aramite 2	185	319	
p-(Dimethylamino)azobenzene	120	225	77

Analyte	Primary	Secondary	Tertiary
p-Chlorobenzilate	251	139	253
3,3'-Dimethylbenzidine	212	106	
2-Acetylaminofluorene	181	180	223
Dibenz(a,j)acridine	279	280	
7,12-Dimethylbenz(a)anthracene	256	241	120
3-Methylcholanthrene	268	252	253

**TABLE 6: Method 8270C LCS Control
Compounds**

LCS Compounds	Spiking Level, Conc. Added = 20 ug/L
1,2,4-Trichlorobenzene	20
Acenaphthene	20
2,4-Dinitrotoluene	20
Pyrene	20
N-Nitroso-di-n-propylamine	20
1,4-Dichlorobenzene	20
Pentachlorophenol	20
Phenol	20
2-Chlorophenol	20
4-Chloro-3-methylphenol	20
4-Nitrophenol	20

TABLE 7

Method 8270C All Analyte Spike Mix	
Acenaphthene	100
Acenaphthylene	100
Anthracene	100
Benzo(a)anthracene	100
Benzo(b)fluoranthene	100
Benzo(k)fluoranthene	100
Benzo(a)pyrene	100
Benzo(ghi)perylene	100
Benzyl butyl phthalate	100
Bis(2-chloroethyl)ether	100
Bis(2-chloroethoxy)methane	100
Bis(2-ethylhexyl)phthalate	100
Bis(2-chloroisopropyl)ether	100

Method 8270C All Analyte Spike Mix	
4-Bromophenyl phenyl ether	100
2-Chloronaphthalene	100
4-Chlorophenyl phenyl ether	100
Chrysene	100
Dibenzo(a,h)anthracene	100
Di-n-butylphthalate	100
1,3-Dichlorobenzene	100
1,2-Dichlorobenzene	100
1,4-Dichlorobenzene	100
3,3'-Dichlorobenzidine	100
Diethyl phthalate	100
Dimethyl phthalate	100
2,4-Dinitrotoluene	100
2,6-Dinitrotoluene	100
Di-n-octylphthalate	100
Fluoranthene	100
Fluorene	100
Hexachlorobenzene	100
Hexachlorobutadiene	100
Hexachloroethane	100
Indeno(1,2,3-cd)pyrene	100
Isophorone	100
Naphthalene	100
N-Nitrosodi-n-propylamine	100
Phenanthrene	100
Pyrene	100
1,2,4-Trichlorobenzene	100
4-Chloro-3-methylphenol	100
2-Chlorophenol	100
2,4-Dichlorophenol	100
2,4-Dimethylphenol	100
2,4-Dinitrophenol	100
2-Methyl-4,6-dinitrophenol	100
2-Nitrophenol	100
4-Nitrophenol	100
Pentachlorophenol	100
Phenol	100
2,4,6-Trichlorophenol	100

Method 8270C All Analyte Spike Mix	
Acetophenone	100
Atrazine	100
Caprolactam	100
Benzaldehyde	100
1,1'-Biphenyl	100
Benzoic Acid	100
1,4-Dioxane	100
Benzyl Alcohol	100
Carbazole	100
4-Chloroaniline	100
Dibenzofuran	100
Hexachlorocyclopentadiene	100
2-Methylnaphthalene	100
1-Methylnaphthalene	100
2-Methylphenol	100
4-Methylphenol	100
4-Nitroaniline	100
2-Nitroaniline	100
3-Nitroaniline	100
Pyridine	100
2,3,5,6-Tetrachlorophenol	100
2,4,5-Trichlorophenol	100
N-Nitrosodimethylamine	100
N-Nitrosodiphenylamine	100

TABLE 8: TCLP LCS Compounds	
LCS Compounds	Spiking Level, mg/L in extract
1,4-Dichlorobenzene	0.08
2,4-Dinitrotoluene	0.08
Hexachlorobenzene	0.08
Hexachlorobutadiene	0.08
Hexachloroethane	0.08
2-Methylphenol	0.08
3-Methylphenol	0.08

4-Methylphenol	0.08
Nitrobenzene	0.08
Pentachlorophenol	0.08
Pyridine	0.08
2,4,5-Trichlorophenol	0.08
2,4,6-Trichlorophenol	0.08

Recovery limits for the LCS and for matrix spikes are generated historical data, and are maintained by the QA Dept.

TABLE 9: Method 8270C Surrogate Compounds	
Surrogate Compounds	Spiking Level, Conc. Added = 20 ug/L / 30 ug/L
Nitrobenzene-d5	20
2-Fluorobiphenyl	20
Terphenyl-d14	20
Phenol-d5	30
2-Fluorophenol	30
2,4,6-Tribromophenol	30

Recovery limits for surrogates are generated from historical data, and are maintained by the QA department.

TABLE 10: Calibration Ranges

Analyte	Calibration Range
Pyridine	0.25-12.5 ug/mL
N-nitrosodimethylamine	0.25-12.5 ug/mL
Aniline	0.25-12.5 ug/mL
Phenol	0.25-12.5 ug/mL
Bis(2-chloroethyl)ether	0.25-12.5 ug/mL
2-Chlorophenol	0.25-12.5 ug/mL
1,3-Dichlorobenzene	0.25-12.5 ug/mL
1,4-Dichlorobenzene	0.25-12.5 ug/mL
Benzyl alcohol	0.25-12.5 ug/mL
1,2-Dichlorobenzene	0.25-12.5 ug/mL

Analyte	Calibration Range
2-Methylphenol	0.25-12.5 ug/mL
2,2'-oxybis(1-chloropropane) ¹	0.25-12.5 ug/mL
4-Methylphenol	0.25-12.5 ug/mL
N-Nitroso-di-n-propylamine	0.25-12.5 ug/mL
Hexachloroethane	0.25-12.5 ug/mL
Nitrobenzene	0.25-12.5 ug/mL
Isophorone	0.25-12.5 ug/mL
2-Nitrophenol	0.25-12.5 ug/mL
2,4-Dimethylphenol	0.25-12.5 ug/mL
Benzoic acid	0.25-12.5 ug/mL
Bis(2-chloroethoxy)methane	0.25-12.5 ug/mL
2,4-Dichlorophenol	0.25-12.5 ug/mL
1,2,4-Trichlorobenzene	0.25-12.5 ug/mL
Naphthalene	0.05-10 ug/mL
4-Chloroaniline	0.25-12.5 ug/mL
Hexachlorobutadiene	0.25-12.5 ug/mL
4-Chloro-3-methylphenol	0.25-12.5 ug/mL
2-Methylnaphthalene	0.05-10 ug/mL
Hexachlorocyclopentadiene	0.25-12.5 ug/mL
2,4,6-Trichlorophenol	0.25-12.5 ug/mL
2,4,5-Trichlorophenol	0.25-12.5 ug/mL
2-Chloronaphthalene	0.25-12.5 ug/mL
2-Nitroaniline	0.25-12.5 ug/mL
Dimethyl phthalate	0.25-12.5 ug/mL
Acenaphthylene	0.05-10 ug/mL
3-Nitroaniline	0.25-12.5 ug/mL
Acenaphthene	0.05-10 ug/mL
2,4-Dinitrophenol	0.25-12.5 ug/mL
4-Nitrophenol	0.25-12.5 ug/mL
Dibenzofuran	0.25-12.5 ug/mL
2,4-Dinitrotoluene	0.25-12.5 ug/mL
2,6-Dinitrotoluene	0.25-12.5 ug/mL
Diethylphthalate	0.25-12.5 ug/mL
4-Chlorophenyl phenyl ether	0.25-12.5 ug/mL
Fluorene	0.05-10 ug/mL
4-Nitroaniline	0.25-12.5 ug/mL
4,6-Dinitro-2-methylphenol	0.25-12.5 ug/mL
N-Nitrosodiphenylamine	0.25-12.5 ug/mL
Azobenzene ²	0.25-12.5 ug/mL

Analyte	Calibration Range
4-Bromophenyl phenyl ether	0.25-12.5 ug/mL
Hexachlorobenzene	0.25-12.5 ug/mL
Pentachlorophenol	0.25-12.5 ug/mL
Phenanthrene	0.05-10 ug/mL
Anthracene	0.05-10 ug/mL
Carbazole	0.05-10 ug/mL
Di-n-butyl phthalate	0.25-12.5 ug/mL
Fluoranthene	0.05-10 ug/mL
Benzidine	0.25-12.5 ug/mL
Pyrene	0.05-10 ug/mL
Butyl benzyl phthalate	0.25-12.5 ug/mL
3,3'-Dichlorobenzidine	0.25-12.5 ug/mL

Analyte	Calibration Range
Benzo(a)anthracene	0.05-10 ug/mL
Bis(2-ethylhexyl)phthalate	0.25-12.5 ug/mL
Chrysene	0.05-10 ug/mL
Di-n-octylphthalate	0.25-12.5 ug/mL
Benzo(b)fluoranthene	0.05-10 ug/mL
Benzo(k)fluoranthene	0.05-10 ug/mL
Benzo(a)pyrene	0.05-10 ug/mL
Indeno(1,2,3-cd)pyrene	0.05-10 ug/mL
Dibenz(a,h)anthracene	0.05-10 ug/mL
Benzo(g,h,i)perylene	0.05-10 ug/mL
Benzaldehyde	0.25-12.5 ug/mL
Caprolactam	0.25-12.5 ug/mL
1,1'-Biphenyl	0.25-12.5 ug/mL
Atrazine	0.25-12.5 ug/mL
2-Picoline	0.25-12.5 ug/mL
N-Nitrosomethylethylamine	0.25-12.5 ug/mL
Methyl methanesulfonate	0.25-12.5 ug/mL
N-Nitrosodiethylamine	0.25-12.5 ug/mL
Ethyl methanesulfonate	0.25-12.5 ug/mL
Pentachloroethane	0.25-12.5 ug/mL
Acetophenone	0.25-12.5 ug/mL
N-Nitrosopyrrolidine	0.25-12.5 ug/mL
N-Nitrosomorpholine	0.25-12.5 ug/mL
o-Toluidine	0.25-12.5 ug/mL

Analyte	Calibration Range
3-Methylphenol	0.25-12.5 ug/mL
N-Nitrosopiperidine	0.25-12.5 ug/mL
o,o,o-Triethyl-Phosphorothioate	0.25-12.5 ug/mL
a,a-Dimethyl-phenethylamine	0.25-12.5 ug/mL
2,6-Dichlorophenol	0.25-12.5 ug/mL
Hexachloropropene	0.25-12.5 ug/mL
p-Phenylenediamine	0.25-12.5 ug/mL
n-Nitrosodi-n-butylamine	0.25-12.5 ug/mL
Safrole	0.25-12.5 ug/mL
1,2,4,5-Tetrachlorobenzene	0.25-12.5 ug/mL
Isosafrole 1 + 2	0.25-12.5 ug/mL
1,4-Dinitrobenzene	0.25-12.5 ug/mL
1,4-Naphthoquinone	0.25-12.5 ug/mL
1,3-Dinitrobenzene	0.25-12.5 ug/mL
Pentachlorobenzene	0.25-12.5 ug/mL
1-Naphthylamine	0.25-12.5 ug/mL
2-Naphthylamine	0.25-12.5 ug/mL
2,3,4,6-Tetrachlorophenol	0.25-12.5 ug/mL
5-Nitro-o-toluidine	0.25-12.5 ug/mL
Thionazin	0.25-12.5 ug/mL
1,3,5-Trinitrobenzene	0.25-12.5 ug/mL
Sulfotepp	0.25-12.5 ug/mL
Phorate	0.25-12.5 ug/mL
Phenacetin	0.25-12.5 ug/mL
Diallate 1 + 2	0.25-12.5 ug/mL
Dimethoate	0.25-12.5 ug/mL
4-Aminobiphenyl	0.25-12.5 ug/mL
Pentachloronitrobenzene	0.25-12.5 ug/mL
Pronamide	0.25-12.5 ug/mL
Disulfoton	0.25-12.5 ug/mL
2-secbutyl-4,6-dinitrophenol (Dinoseb)	0.25-12.5 ug/mL
Methyl parathion	0.25-12.5 ug/mL
4-Nitroquinoline-1-oxide	0.25-12.5 ug/mL
Parathion	0.25-12.5 ug/mL
Isodrin	0.25-12.5 ug/mL
Kepone	0.25-12.5 ug/mL
Famphur	0.25-12.5 ug/mL
Methapyrilene	0.25-12.5 ug/mL

Analyte	Calibration Range
Aramite 1 and 2	0.25-12.5 ug/mL
p-(Dimethylamino)azobenzene	0.25-12.5 ug/mL
p-Chlorobenzilate	0.25-12.5 ug/mL
3,3'-Dimethylbenzidine	0.25-12.5 ug/mL
2-Acetylaminofluorene	0.25-12.5 ug/mL
Dibenz (a,j)acridine	0.25-12.5 ug/mL
7,12-Dimethylbenz(a)anthracene	0.25-12.5 ug/mL
3-Methylcholanthrene	0.25-12.5 ug/mL

¹ 2,2'-oxybis(1-chloropropane) was formerly known as bis(2-chloroisopropyl)ether.

² Azobenzene is formed by decomposition of 1,2-diphenylhydrazine. If 1,2-diphenylhydrazine is requested, it will be analyzed as azobenzene.

Note: Nine calibrations standards are prepared varying in concentration from 0.05 ug/mL to 12.5 ug/mL. A minimum of 5 calibration concentrations will be used for initial calibration. The concentration range of each analyte is listed in the table.

Table 11A: Method 8270D Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION		
1,4-Dichlorobenzene-d ₄	Naphthalene-d ₈	Acenaphthene-d ₁₀
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl- phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Nitrobenzene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	Nitrobenzene-d ₈ (surr)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitrosodi-n-butylamine	2-Nitroaniline
Phenol-d ₆ (surr)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetrachlorobenzene
		2,3,4,6-Tetrachlorophenol
		2,4,6-Tribromophenol (surr)
		2,4,6-Trichlorophenol
		2,4,5-Trichlorophenol

(surr) = surrogate

Phenanthrene-d ₁₀	Chrysene-d ₁₂	Perylene-d ₁₂
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
Fluoranthene	p-Dimethyl aminoazobenzene	7,12-Dimethylbenz(a)anthracene
Hexachlorobenzene	Pyrene	Di-n-octyl phthalate
N-Nitrosodiphenylamine	Terphenyl-d ₁₄ (surr)	Indeno(1,2,3-cd) pyrene
Pentachlorophenol		3-Methylcholanthrene
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr) = surrogate

Table 11B: Method 8270C Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

1,4-Dichlorobenzene-d4	Naphthalene-d8	Acenaphthene-d10
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	Acenaphthene
Bis(2-chloroisopropyl)ether	2,4-Dichlorophenol	Acenaphthylene
2-Chlorophenol	2,4-Dimethylphenol	2-Chloronaphthalene
1,2-Dichlorobenzene	Hexachlorobutadiene	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	Isophorone	Diethyl phthalate
1,4-Dichlorobenzene	Nitrobenzene	Dimethyl phthalate
2-Fluorophenol (surrogate)	Nitrobenzene-d ₈ (surrogate)	2,4-Dinitrophenol
Hexachloroethane	2-Nitrophenol	2,4-Dinitrotoluene
N-Nitroso-di-n-propylamine	1,2,4-Trichlorobenzene	2,6-Dinitrotoluene
Phenol		Fluorene
Phenol-d6 (surrogate)		2-Fluorobiphenyl (surrogate)
		4-Nitrophenol
		2,4,6-Tribromophenol (surrogate)
		2,4,6-Trichlorophenol

Table 11C: Semivolatile Internal Standards with Corresponding Analytes Assigned for Quantitation

Phenanthrene-d10	Chrysene-d12	Perylene-d12
Anthracene	Benzo(a)anthracene	Benzo(b)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl)phthalate	Benzo(k)fluoranthene
Di-n-butyl phthalate	Chrysene	Benzo(g,h,i)perylene
4,6-Dinitro-2-methylphenol	3,3'-Dichlorobenzidine	Benzo(a)pyrene
Fluoranthene	Pyrene	Dibenz(a,h)anthracene
Hexachlorobenzene	Terphenyl-dl4 (surrogate)	Di-n-octylphthalate
Pentachlorophenol		Indeno(1,2,3-cd)pyrene
Phenanthrene		3-Methylcholanthrene

Table 12: Recommended Minimum Response Factor Criteria for Initial and Continuing Calibration Verification

Semivolatile Compounds	Minimum Response Factor (RF)
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitros-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactum	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Dithyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010

Semivolatile Compounds	Minimum Response Factor (RF)
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

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**

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

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

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
 - o Dip into distilled water for 1 second, shake off excess water, or
 - o 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.

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.

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

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

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 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:

Waters

1L Amber Glass – purchased with Certificate of Analysis attesting to purity.

Soils

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

- 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 (H₂SO₄) – 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

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 $\frac{3}{4}$ 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

- 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.

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

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

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

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 days 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

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

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)

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.

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.

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

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.

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 $\frac{3}{4}$ 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.

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)

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*.

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 of 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.

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 "OD", 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

deviation, relative standard deviation, relative response factor, and relative standard deviation.

11.2.3 The calculation to determine final concentration is given as follows:

$$FinalConcentration = CONC_{Sample} \otimes \frac{F}{I \times dw} \otimes D$$

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).

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

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.

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 Pentafluorobenzoylation 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.

16.1.1 Waste Samples

Waste samples are extracted as follows:

Weigh 1.0-1.2g of the homogenized sample into a calibrated 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

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 MeCl ₂ . Shake each aliquot for 2 minutes.	1x100mL MeCl ₂ . 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.

- 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

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 \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.

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.

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

**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 \leq 10%; $r^2 > 0.990$ EPA 515.1 and 8151A: $< 20\%$ RSD; $r^2 > 0.990$	Refer to SOP SA-QA-16
2 nd Source Initial Calibration Verification (ICV)	After Initial Calibration. (Quarterly, at a minimum, for EPA 515.1)	EPA 515.1: Percent difference $\leq 20\%$ EPA 615 and 8151A: Percent difference $\leq 15\%$ 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 $\pm 20\%$ 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 $\pm 10\%$ of the true value	
	EPA 8151A: At the beginning and end of the analysis, and every 12 hours or 20 samples	Within $\pm 15\%$ of the true value; GME with no single analyte $> 45\%$	

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	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Matrix Spike Duplicate (MSD)	EPA 8151A: One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
Surrogate	One per batch	Within limits listed in the MLG	Evaluate according to SOP SA-QA-17
	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

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

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.

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.

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
Dinoseb	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).

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-Dichlorobenzoic 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)

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

**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.

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.

18.0 Revision History

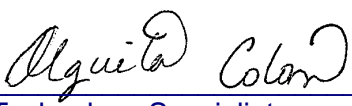

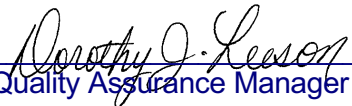

Summary of Changes from Previous Revision:

- 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)

Title: pH ELECTROMETRIC METHOD

**[Method: SW846 Methods 9040B, 9040C, 9041A, and 9045C, EPA
Method 150.1, SM4500 H⁺B]**

Approvals (Signature/Date):

 Technology Specialist	<u>04/03/12</u> Date	 Health & Safety Coordinator	<u>04/04/12</u> Date
 Quality Assurance Manager	<u>04/13/12</u> Date	 Laboratory Director	<u>04/16/12</u> Date

This SOP was previously identified as SOP NC-WC-010, Rev 10 dated 11/24/10

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of pH in waters, wastewaters, and solids. It is based on SW846 Methods 9040B, 9040C, 9041A, and 9045C, SM4500 H⁺B, and EPA Method 150.1. Method 9040B/9040C should be used if the aqueous phase constitutes at least 20% of the total volume of the waste. Method 9045C should be used for measuring pH in soils and waste samples. If water is present, it must constitute less than 20% of the total volume of the sample. See Section 11 for details on determining the correct method.
- 1.2. The approximate working range is 1 - 14 pH units. Samples with a pH of < 1 are reported as < 1.
- 1.3. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

- 2.1. The pH is determined electrometrically by using an electrode. The pH meter is calibrated with a series of known pH buffers.
- 2.2. For Method 9041A, an aliquot of sample is analyzed for pH using pH paper. Samples are mixed with water prior to analysis.

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

- 4.1. Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low sodium error electrode.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

- 5.2. There are no materials used in this method that have a serious or significant hazard rating.
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.
- 5.3. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately
- 5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.6. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents should be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.7. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. pH meter with electrode(s) and temperature compensation
- 6.2. Beakers: various
- 6.3. Top loading balance: Capable of accurately weighing ± 0.01 g
- 6.4. Stir plate and stir bars
- 6.5. Shaker or mechanical tumbler

- 6.6. Autotitrator
- 6.7. Centrifuges tubes
- 6.8. pH paper: Various pH ranges
- 6.9. Disposable snap top containers

7. REAGENTS AND STANDARDS

- 7.1. Standards
 - 7.1.1. A commercially available control standard (LCS).
 - 7.1.2. Target Calibration Standards
 - 7.1.2.1. pH 2, 4, 7, 10, and 12 buffers--purchased
 - 7.1.2.2. Fresh buffers are poured and used each working day.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1. Samples are not chemically preserved.
- 8.2. Samples are stored in plastic or glass containers at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$.
- 8.3. Samples should be analyzed as soon as possible after sampling, but not to exceed one day after sampling.

9. QUALITY CONTROL

- 9.1. Batch Definition
 - 9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (LCS and Sample Duplicate) which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Sample Duplicate

- 9.2.1. A sample duplicate (DU) is a second aliquot of an environmental sample, taken from the same sample container when possible, that is processed with the first aliquot of that sample. That is, sample duplicates are processed as independent samples within the same QC batch. The sample and DU results are compared to determine the effect of the sample matrix on the precision of the analytical process. As with the MS/MSD results, the sample/DU precision results are not necessarily representative of the precision for other samples in the batch.
- 9.2.2. Sample duplicates are performed at a frequency of 10% per matrix, and must meet laboratory-specific limits for precision. For 9041A, all samples will be analyzed in duplicate.

9.3. Laboratory Control Sample (LCS)

- 9.3.1. One aqueous LCS must be processed with each analytical batch. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.
- 9.3.2. A commercially available (Environmental Resource Associates or equivalent) control standard will be analyzed. Recovery must be within +/-3% of true value.
- 9.3.3. Corrective Action for LCS
 - 9.3.3.1. If the pH is outside the established control limits the system is out of control and corrective action must occur.
 - 9.3.3.2. Corrective action consists of identification and correction of the cause for the out of control situation and reanalysis of all effected samples.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

- 10.1.1. Refer to the manufacturer's manual for instrumental calibration.
- 10.1.2. Corrosivity analysis under 9040B and C require differing calibration buffers. Reference section 10.1.3 for pH, and section 10.1.4 for Corrosivity.

10.1.3. The following procedure is applicable for use with the Orion 320 pH meter.

10.1.3.1. If in “Standby” mode, press “Mode”. Rinse the electrodes with reagent water and place in the pH 7 buffer. Press “Cal”. When 7.4 is displayed, press “yes”. Allow to stabilize. When “Ready” light comes on, press “yes”.

10.1.3.2. Rinse electrode with reagent water, and place in pH 4 buffer. When “Ready” light comes on, press “yes”. Record electrode slope on analytical logsheet.

10.1.3.3. Methods 9040B and C requires a calibration buffer of pH 2 and pH12 if corrosivity characterization is needed.

10.1.3.4. Calibration Check: Rinse the electrodes and place in the pH 10 buffer. Allow value to stabilize. The pH should be between 9.95 and 10.05 or recalibration is necessary.

10.1.3.5. After calibration, run a pH 7, a pH 2, a pH 12, then an LCS, allowing the electrode to stabilize for each. Record results on analytical logsheet.

10.1.4. For 9040B and C Corrosivity, use the Mettler Toledo S20 pH meter for narrow range sample readings.

10.1.4.1. The S20 pH meter will require calibration dependant upon the sample’s initial pH reading from the Orion 320.

10.1.4.2. Chose an appropriate 3 point calibration range (2, 4, and 7 or 7, 10, and 12) from the calibration menu.

10.1.4.2.1. Place the probe in the first calibrant and press “Cal”.

10.1.4.2.2. Rinse the probe with DI water, place the probe in the second calibration buffer and press “Cal”.

10.1.4.2.3. Repeat with the 3rd calibration buffer.

NOTE: Between every two calibration points, the instrument will define the offset and the slope. Manufacturer’s recommended criteria for the offset is $\pm 15\%$, and slope criteria is 95 – 105. A three-point calibration will have two values for offset and slope. If either of these values fall outside of the manufacturer’s criteria, recalibration is required.

10.1.3 The pH meter must be calibrated daily. The calibration is recorded on the analytical logsheet.

10.1.4 If the pH meter has been turned off, it must be calibrated prior to use.

10.2. Continuing Calibration

10.2.1. For pH: A pH 7 buffer is analyzed before sample analysis, every ten samples, and at the end of the analysis to ensure the calibration remains linear.

10.2.2. For Corrosivity: Continuing Calibration level is dependant upon which level calibration curve is used. Samples analyzed for Corrosivity must be bracketed by the mid-point buffer from the calibration curve used for the sample. For example, a sample(s) with an initial value of 3.5 must be bracketed by passing pH 4 buffer checks.

10.2.3. The pH meter must be recalibrated if the buffer deviates by more than ± 0.05 . If this range is exceeded, re-analyze all samples analyzed since the last pH buffer that met criteria.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo. The Nonconformance Memo shall be filed in the project file.

11.2. Sample Preparation

11.2.1. At the time of sample receipt, the sample must be inspected to determine the correct method reference. General Chemistry staff members will determine the percent of aqueous phase present and notify the Sample Receiving staff if a method change is needed. The Sample Receiving staff will notify the Project Manager to make the appropriate change in LIMS. Method 9040B should be used if the aqueous phase constitutes at least 20% of the total volume of the waste. Method 9045C should be used for measuring pH in soils and waste samples. If water is present, it must constitute less than 20% of the total volume of the sample.

NOTE: The analyst will note in the comments section in LIMS which method was used and if a method change was required.

11.2.2. Waters

11.2.2.1. No preparation necessary for waters and wastewaters.

11.2.3. Solids and Soils

11.2.3.1. Place 10 g (\pm 0.5 g) of sample in a beaker or other suitable container.

11.2.3.2. Add 10 mL of reagent water and mix for five minutes in a shaker or mechanical tumbler.

11.2.3.3. Allow sample to stand for one hour to allow the solids to settle out.

11.2.4. Waste

11.2.4.1. Place 10 g (\pm 0.5 g) of sample in a beaker or other suitable container.

11.2.4.2. Add 10 mL of reagent water and mix for five minutes in a shaker or mechanical tumbler.

11.2.4.3. Let the waste suspension stand for about 15 minutes to allow most the suspended waste to settle out from the suspension or filter or centrifuge off aqueous phase for pH measurement.

Note: If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase. The electrode may need to be cleaned if it becomes coated with an oily material.

11.2.5. Method 9041A Sample Preparation (solids, sludges, and oils)

11.2.5.1. Place 10 g (\pm 0.5 g) of sample in a snap cap.

11.2.5.2. Add 10 mL of reagent water to the sample and mix.

11.2.5.3. Allow the sample and water layers to separate and carefully decant the water layer into another snap cap for analysis. If it is not possible to decant without decanting some of the sample (in the case of oils or oily sludges), it is permissible to use a disposable transfer pipette to remove the water layer for analysis.

11.3. Sample Analysis

11.3.1. Manual Procedure

11.3.1.1. Waters

11.3.1.1.1. Place the sample in a clean beaker using a sufficient volume to cover the sensing elements of the electrode(s). Allow the pH to stabilize (swirling or stirring may quicken stabilization). Record the pH on the analytical logsheet. Remove the electrodes from the sample. Rinse and gently dab off the electrodes between each measurement. Store the electrodes in pH 7 buffer when not in use.

NOTE: If Corrosivity is requested, calibrate the Mettler Toledo S20 pH Meter according to the procedure listed in 10.1.4, and continue analyzing following steps 11.3.1.1.2 and 11.3.1.1.3 on that instrument.

11.3.1.1.2. For 9040B, 9040C, and 150.1 – Continuously stir the sample while obtaining a stable reading.

11.3.1.1.3 For Method 9040B, 9040C and 150.1 note and record the sample pH of the first aliquot. Repeat the measurement on successive aliquots of sample until the values differ by < 0.1 pH units. Two or three volume changes are usually sufficient. If more than three measurements are required, contact the Group Leader.

11.3.1.2. Solids

11.3.1.2.1. Immerse the pH electrodes in the supernatant layer of the sample - be careful not to stir up solids. Allow pH to stabilize and record it on the analytical logsheet. Remove and rinse the electrodes between each measurement. Store electrodes in the pH 7 buffer.

NOTE: If the sample contains oil or other substances that will coat or damage the electrodes, the pH should be analyzed by pH - Paper Method 9041A.

11.3.2. Automated Procedure

11.3.2.1. Load the appropriate schedule on the autotitrator starting with the pH calibration.

11.3.2.2. Pour a homogenized sample into the centrifuge tubes and place the tubes in the appropriate position on the autosampler. Remember to include a pH 7 buffer check after every ten positions.

11.3.2.3. Start the autotitrator.

11.3.3. Method 9041A Sample Analysis Procedure

11.3.3.1. Immerse the wide range pH paper into the decanted water layer of the sample for several seconds. Remove the paper and determine the pH range from the manufacturer's pH chart. Using the appropriate narrow range pH paper, read the sample pH and record the pH on the analytical logsheet. Reading with the narrow range pH paper will be done in duplicate.

NOTE: The initial pH range check that is performed with the wide range pH paper does **not** count as a duplicate analysis.

11.4. Analytical Documentation

11.4.1. Record all analytical information in LIMS, including the analytical data from standards and any corrective actions or modifications to the method.

11.4.2. All standards are logged into the LIMS standard and reagent module. All standards are assigned a unique number for identification.

11.4.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs are scanned and attached to the Documents section in the LIMS analytical batch.

11.4.4. Sample results and associated QC are transferred directly into LIMS at the time of analysis. Level I and Level II review is done in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not Applicable

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. 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".

15. WASTE MANAGEMENT

15.1. 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 Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Waste Streams Produced by the Method

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

15.2.1.1. Acidic and alkaline sample waste and exhausted buffer solutions can be poured down the drain if the pH is between 5 and 10. Any sample waste generated that is not in this pH range is collected in a designated container identified as "Acid Waste".

15.2.1.2. Exhausted soil or oil samples analyzed by the method. The liquid layer is decanted and disposed of in a designated container identified as "Acid Waste". The remaining solid layer is disposed of by placing it in a container identified as "Solid Waste".

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these

tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, pH Electrometric Measurement, Method 9040B

16.1.2. EPA 600, Methods for Chemical Analysis of Water and Wastes, pH (Electrometric), Method 150.1

16.1.3. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Soil pH, Method 9045C

16.1.4. SW846, Test Methods for Evaluating Solid Waste, pH Electrometric Measurement, Method 9040C, Revision 3, August 2002.

16.1.5. SW846, Test Methods for Evaluating Solid Waste, Third Edition, pH paper, Method 9041A.

16.1.6. Standard Method for pH Electrometric Method, Eighteenth Edition, SM4500 H⁺B

16.1.7. [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version

16.1.8. TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version

16.1.9. [Corporate Quality Management Plan \(CQMP\)](#), current version

16.1.10. Revision History

Historical File:		Revision 4.0: 01/04/99		Revision 10: 11/24/10
		Revision 4.1: 11/28/00		
		Revision 5: 02/05/03		
		Revision 6: 10/27/04		
		Revision 7: 03/23/06		
		Revision 8: 04/30/08		
		Revision 9: 05/26/10		

16.2. Associated SOPs and Policies, current version

16.2.1. QA Policy, [QA-003](#)

16.2.2. Glassware Washing, [NC-QA-014](#)

16.2.3. Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)

16.2.4. Supplemental Practices for DoD Project Work, [NC-QA-016](#)

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. A minimum reporting limit of 0.1 SU (standard units) is listed in LIMS. Units are reported as “SU”.

17.2. Method Deviations

17.2.1. Method 9041A requires a procedure to identify interferences. The laboratory does not perform this procedure.

17.2.2. Method 9041A requires each batch of pH paper to be calibrated versus certified pH buffers or a pH meter which has been calibrated with certified pH buffers. The pH paper is not calibrated by the laboratory.

17.2.3. Method 9041A does not call for any kind of sample preparation, however, due to the various matrices encountered, the laboratory preps the samples as described in section 11.2.5.

Title: PAINT FILTER

[Method: SW846 Method 9095A and 9095B]

Approvals (Signature/Date):


Technology Specialist 08/20/12
Date


Health & Safety Coordinator 08/20/12
Date


Quality Assurance Manager 08/20/12
Date


Laboratory Director 08/20/12
Date

This SOP was previously identified as SOP No. NC-WC-046, Rev 4, dated 4/5/11

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of the presence of free liquid in a variety of wastes. It is based on SW846 Methods 9095A and B.
- 1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory.

2. SUMMARY OF METHOD

- 2.1. An aliquot of sample is placed in a paint filter. If any portion of the material passes through the filter in five minutes, the sample is deemed to contain free liquids.

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

- 4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.
- 5.2. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.3. There are no materials used in this method that have a serious or significant hazard rating. **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.

- 5.4. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.
- 5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and the laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Conical paint filter: Mesh 60 x 48
- 6.2. Glass funnel
- 6.3. Ring stand
- 6.4. 100 ml Graduated cylinders

7. REAGENTS AND STANDARDS

- 7.1. Not applicable

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1. Samples are not chemically preserved.
- 8.2. Samples are stored in glass containers at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$.
- 8.3. Holding Times - Not Applicable

9. QUALITY CONTROL

- 9.1. Duplicates
 - 9.1.1. Sample duplicates are performed at a minimum frequency of 10% (or one per analytical batch of 20) and must meet laboratory-specific limits for precision.

10. CALIBRATION AND STANDARDIZATION

10.1. Not applicable

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Non-conformance Memo.

11.2. Any unauthorized deviations from this procedure must also be documented as a non-conformance, with a cause and corrective action described.

11.3. Sample Preparation

11.3.1. Not applicable

11.4. Sample Analysis

11.4.1. Place an aliquot of representative sample (approximately 100 ml or 100 g) in the paint filter, which is placed in the glass funnel above a graduated cylinder.

11.4.2. Allow the sample to drain for five minutes into the graduated cylinder. If any free liquid is collected in the graduated cylinder, the sample is considered positive. If no free liquid is collected, the sample is negative. Data entry into LIMS is POS for Positive and NEG for Negative.

NOTE: If sample quantity is limited, a visual procedure may be performed and documented accordingly.

11.5. Analytical Documentation

11.5.1. Record all analytical information in LIMS, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

11.5.2. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) is available for each data file.

11.5.3. Sample results are entered into LIMS. Level I and Level II technical reviews are done in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Training Qualifications

13.1.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. 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".

15. WASTE MANAGEMENT

15.1. 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 Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.2. Solid materials (gloves, soiled paper products, etc.) are placed in the solid debris container. Do not put liquids in the solid waste container.

15.3. Refer to the Laboratory Sample and Waste Disposal plan.

15.4. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica Canton. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

15.5. Waste Streams Produced by the Method

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

15.5.1.1. Spent sample is to be disposed of in the non-hazardous solids container located in the prep lab near the sink.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Paint Filter Liquids Test, Method 9095A

16.1.2. SW846, Test Methods for Evaluating Solid Waste, Method 9095B, Revision 2, August 2002

16.1.3. [Corporate Quality Management Plan \(CQMP\)](#), current version

16.1.4. [TestAmerica Canton Quality Assurance Manual](#) (QAM), current version

16.1.5. TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and [TestAmerica Canton Facility Addendum and Contingency Plan](#), current version

16.1.6. Revision History

Historical File:		Revision 0: 06/08/95		Revision 4: 04/05/11
		Revision 1: 09/25/03		
		Revision 2: 10/30/07		
		Revision 3: 12/31/09		

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Method Deviations

17.1.1. SW846 Method 9095 requires a paint filter size 60 mesh. This size is no longer commercially available. Mesh size 60 x 48 has been deemed acceptable by the EPA, and will be used for analysis.

**IH Air Method for Total & Respirable Dusts & Carbon Black
[Method No(s). Modified NIOSH 0500, 0600 & 5000]**

Approvals (Signature/Date):



Stephanie Stimson
Industrial Hygiene Department Manager

6/15/2010

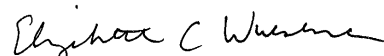
Date



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6/15/2010


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Date

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1.0 Scope and Application

- 1.1 This standard operating procedure (SOP) is appropriate for the gravimetric determination of total dusts by NIOSH 0500, respirable dusts by NIOSH 0600, and carbon black by NIOSH 5000.
- 1.2 The validated methods have been modified to use an analytical balance with readability of 0.01 mg instead of 0.001 mg.
- 1.3 The reporting level (RL) for total dusts, respirable dusts and carbon black is 0.1 mg/sample (100 µg/sample).

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 7.3.1 in the Quality Assurance Manual.

2.0 Summary of Method

- 2.1 Total dusts and carbon black are sampled by pulling air through a 37-mm closed –face polystyrene cassette containing a 37-mm pre-weighed PVC filter (with support pad). Respirable dusts are sampled by pulling air through an aluminum cyclone attached to the front of an open-faced 37-mm cassette containing a 37-mm pre-weighed PVC filter (with support pad). Air is pulled through the samples by use of a personal sampling pump at 1 – 2 L/min for respirable dust sampling using the aluminum cyclone.

3.0 Definitions

- 3.1 Initial Calibration Standards (ICAL) – A series of CAL solutions used to initially establish instrument calibration and develop calibration curves.
- 3.2 Reporting Level Calibration Check Standard (RL CK) - A spiked filter, which is analyzed initially, prior to any field sample analysis, which verifies the established reporting level. The concentration for the RL CK should be at the reporting level calibration level, 100 µg/sample (0.1 mg/sample).
- 3.3 Continuing Calibration Verification Standard (CCV) – A CAL solution which is analyzed after every tenth field sample analysis, not including QC samples, which verifies the previously established calibration curve and confirms accurate analyte quantitation for the previous field samples analyzed. The concentration of the CCV should be at the 1 mg external calibration level.
- 3.4 Laboratory Control Sample / Laboratory Control Sample Duplicate (LCS / LCSD) – An aliquot of reagent water, or other blank matrix, to which a known quantity of analyte is added in the laboratory. The LCS/LCSD are analyzed exactly like a sample.

- 3.5** Method Blank (MB) – A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses.
- 3.6** Relative Percent Difference (RPD) – the difference between two values divided by the average of the values as expressed as a percent.
- 3.7** Accuracy – The degree of agreement of a measured quality of concern.
- 3.8** Precision – The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. It is concerned with the closeness of results.
- 3.9** Initial Demonstration of Capability (IDC) – A procedure to establish the ability of the analyst to generate acceptable accuracy and precision.
- 3.10** Batch – A batch is a group of samples, prepared and/or analyzed together with the same process (i.e. a single work shift).
- 3.11** Refer to the Quality Assurance Manual, Appendix 2 Glossary/Acronyms for additional definitions and terms not defined in this section.

4.0 Interferences

- 4.1** Static may cause difficulties when trying to remove the PVC filter from the cassette. An antistatic radiation source may be used to eliminate this problem, if necessary.

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** There are no specific safety concerns or requirements for this method.

5.2 Primary Materials Used

- 5.2.1** There are no 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.** A complete

list of materials used in the method can be found in the reagents and equipment section. Employees must review the information in the MSDS for each material before using it for the first time and when there are major changes to the MSDS.

6.0 Equipment and Supplies

6.1 Instrumentation

- Sartorius Balance, Model CP225D.
- Static Neutralizer

6.2 Supplies

- Pre-weighed Polyvinyl Chloride (PVC) filter, 3-piece cassette, 37-mm in diameter, 5- μ m pore size, available from Zefon International (catalog number 7P53P, or equivalent).
- 37-mm in diameter, 5- μ m pore size PVC filters, loose. Available from Zefon International (catalog number FPVC537, or equivalent).
- Cellulose support pads: 37-mm. Available from Zefon International (catalog number FSP37, or equivalent).
- Cassette opener available from SKC (catalog number 225-13-5, or equivalent).
- 37-mm Aluminum cyclone available from SKC (catalog number 225-01-02, or equivalent).
- Aluminum Calibration Chamber available from SKC (catalog number 225-01-03, or equivalent).
- Personal sampling pump, capable of flows between 1 to 3 L/min., with flexible connecting tubing.
- Filter cassette holder available for SKC (catalog number 225-1, or equivalent).
- Dorr-Oliver Nylon Cyclone
- Calibration Jar
- Forceps (Preferably Nylon)
- Weights, NIST Class S-1.1, or ASTM Class 1

7.0 Reagents and Standards

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of determination.

7.1.1 Life of Reagents: Reference the current version of SOP PE-QAD-013.

7.2 Sodium Chloride (NaCl).

7.3 Deionized (DI) Water.

8.0 Sample Collection, Preservation, Shipment and Storage

- 8.1 Sample should be transported sealed to the laboratory following sampling. There are no special storage requirements. Once the samples are received at the laboratory they are stored in the file cabinet in the SVOA lab by the IH hoods.
- 8.2 For instructions on preparing the sample cassettes (pre-weigh), see **Procedure** Section.

9.0 Quality Control

QC Performed	Frequency	Acceptance Criteria	Corrective Action
Internal Calibration	Every day before first use	Sartorius balance is self-calibrating and will display 0.00000 g when calibrated	1) Turn balance on and off to reset 2) Consult manual 3) Perform maintenance
100 mg and 10 mg External Calibration Weights	Immediately after internal calibration and prior to weighing filters or samples	Within $\pm 1\%$ of expected value	1) Remove weight, tare balance again and re-weigh 2) Perform Internal Calibration 3) Perform maintenance
1 mg External Calibration Weight	Immediately after internal calibration and prior to weighing filters or samples	Within $\pm 1\%$ of Expected value	1) Remove weight, tare balance again and re-weigh 2) Perform Internal Calibration 3) Perform maintenance
CCV (1-mg External Calibration Weight)	Every 60 weight readings and at the end of the analysis batch	Within $\pm 1\%$ of Expected value	1) Remove weight, tare balance again and re-weigh 2) Ensure there is no static interference 3) Perform maintenance
Field Blank	One per batch of samples (if supplied by client)	< Reporting Limit	1) Include in report 2) Comment in report if a field blank was not submitted
LCS/LCSD 150 – 200 μg NaCl loaded onto each filter spike	LCS and LCSD with each batch of samples	50 to 150% Accuracy and $\leq 50\%$ RPD until historical limits are established	1) Re-weigh the LCS/LCSD 2) Prepare and weigh new LCS/LCSD 3) Flag data
Reporting Level Calibration Check 100 μg NaCl spiked onto filter	With each batch of samples	50 to 150% Accuracy and $\leq 50\%$ RPD	1) Re-weigh the RL CK 2) Prepare and weigh new RL CK 3) Increase reporting level-if necessary

- 9.1 Field Blank. A field blank should be submitted with each batch of samples.
- 9.2 Laboratory Control Sample and Laboratory Control Sample Duplicates (LCS/LCSD)

- 9.2.1** An LCS/LCSD should be prepared with each sample batch (post-weighting process) to ensure that the system is in control when samples are being analyzed.
- 9.2.2** Pre-weigh each filter to be used for the LCS and LCSD. The spiking solution is prepared by accurately weighing NaCl crystals onto a vial on the balance. Add deionized water to the vial to dissolve the salt crystals. For example, 0.1000 grams of salt dissolved in 2.5 mL of water yields a spiking solution equivalent to ~50 µg NaCl/µL. Spike 4 µL of spiking solution onto each filter (~150 – 200 µg NaCl) in a cassette and allow the spike to dry (dry overnight, in a oven, or until the water droplet is no longer visible). Once the two spikes are dry, post-weigh them (see **Procedure** Section 3.), and record the weights. The difference in pre and post weights is assumed to be the NaCl that was spiked on the filter. Acceptable limits are 50 –150% accuracy and ≤ relative percent difference (RPD) or historical limits once they are established.

9.3 Method Blank

- 9.3.1** A method blank must be analyzed with each batch of samples. Extract and analyze at least one passive monitor as described in this SOP.
- 9.3.2** Most analytes found in the method blank will generally be below the reporting levels. However, if there is a value above the reporting level, then subtract the blank from the QC samples and the client's samples. If the method blank yields a result above the reporting level, but the client's samples do not show a background or the QC samples do not have an unusually high recovery, then the contamination is most likely isolated to that blank and further investigation should occur and an appropriate decision be made after further investigation. An appropriate decision may include, but not be limited to, re-analyzing the blank, extracting one or two additional blanks, analyzing an additional aliquot of the solvent used for extraction to check for contamination, ignoring the blank if it is obviously the only sample contaminated, etc.

10.0 Procedure

10.1 Sample Preparation

- 10.1.1** Sample Analysis (post-weight). Calibrate the balance as in section 9.2.
- 10.1.2** Wipe dust from the external surface of the filter cassette with a moist paper towel or Kim Wipe to minimize contamination. Discard the paper towel/Kim wipe.
- 10.1.3** Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in the balance room.

10.2 Calibration

- 10.2.1** Prior to weighing filters, calibrate the balance (Refer to SOP PE-QAD-016 Balance Calibration Care and Use, current revision), and check it against external standard weights.

10.2.2 If the balance was not used earlier in the day, internally calibrate it first. Turn the balance on and allow it to stabilize. Tare the balance, if necessary. Start calibration by pressing the "CAL" button and allow the balance to internally calibrate itself. The balance should return to a display of 0.00000 grams. It is now ready for the external calibration check. Consult the manual if there are concerns or problems with the calibration steps.

10.2.3 External calibration check. Weigh 3 different NIST certified weights. The weights are 100 mg, 10 mg, and 1 mg. The 100 mg and 10 mg weights must be within $\pm 1\%$ of the nominal values, and the 1 mg weight must be within $\pm 1\%$ of the nominal weight. Record the calibration check results in the balance logbook.

10.3 If the balance was internally calibrated earlier in the day, only an external calibration check is performed before using the balance. If the external calibration checks fail, perform the internal calibration again along with the external calibration checks. If the external checks pass, proceed with weighing filters or samples. If the external checks fail, the balance may need servicing. Discuss options with the Quality Assurance department.

10.4 Sample Analysis

10.4.1 Remove the cassette band, pry open the cassette, and remove the filter gently to avoid loss of dust using forceps.

NOTE: If the filter adheres to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

10.4.2 Zero the microbalance before all weighings.

10.4.3 Analyze the filter two times. Subtract the pre-weight average from the post-weight average. The difference in weight is assumed to be dust, which is used to calculate the air concentrations for total dusts, or respirable dusts or carbon black (whenever was being sampled).

11.0 Calculations/ Data Reduction

11.1 Data Review Checklist, see **Table 1**.

11.2 Report results and all QC samples to two significant figures.

11.3 Refer to **Table 2** and **Table 3** for examples of the logbook sheets.

11.4 Determine the mass, μg found on the filter by subtracting the pre-weight filter average from the post-weight filter average.

$$\text{grams} / \text{sample} = \text{Post} - \text{Pre}$$

Where:

Post = Post-weight filter average (in grams)

Pre = Pre-weight filter average (in grams)

11.5 Calculate the air concentration as follows:

$$mg/m^3 = \frac{Ma \times 1,000,000}{V}$$

Where:

mg/m³ = Milligrams per cubic meter (these units used per IH guideline)
Ma = Grams/sample (calculated in previous step)
V = Volume of air pulled through sample in liters
1,000,000 = Conversion from grams/sample to µg/sample

11.6 **Accuracy**

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

11.7 **Precision (RPD)**

$$\text{Relative Percent Difference (RPD)} = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

11.8 **Mean (\bar{x})**: Adding together the numerical values (a, b, c, etc.) of an analysis and dividing this sum by the number *n* of measurements used yields the mean.

$$\bar{x} = \frac{a + b + c}{n}$$

11.9 **Percent Recovery (% Recovery)**.

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike sample result
SR = Sample result
SA = Spike added from spiking standard

12.0 **Method Performance**

12.1 Method Detection Limit Study (MDL). The MDL must be established initially, whenever there is a significant change in instrument response. Spike seven replicate filters with

aliquots of NaCl at one to five times the estimated detection limit (100 µg is the expected reporting limit) and process through the entire analytical method.

12.1.1 The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in Section 19.7 of the QA Manual. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.1.2 MDL is also sometimes referred to as Limit of Detection (LOD).

- I. "The validity of the LOD shall be confirmed by qualitative identification of the analyte(s) in a QC sample in each quality system matrix containing the analyte at no more than 2-3X the LOD for single analyte tests and 1-4X the LOD for multiple analyte tests. The verification must be performed on every instrument that is to be used for analysis of samples and reporting of data." (2003 NELAC Standards, C.3.1.b)

12.1.3 An important characteristic of expression of sensitivity is the difference in the MDL (LOD) and the Quantitation Limit or Reporting Limit (sometimes referred to as the Limit of Quantitation (LOQ)). (NELAC Requirement)

- I. "The validity of the LOQ shall be confirmed by successful analysis of a QC sample containing the analytes of concern in each quality system matrix 1-2 times the claimed LOQ. A successful analysis is one where the recovery of each analyte is within the established test method acceptance criteria or client data quality objective for accuracy. This single analysis is not required if the bias and precision of the measurement system is evaluated at the LOQ." (2003 NELAC Standards, C.3.2.c)

12.1.4 Additional information can be found in Section 19 of the QA Manual.

12.2 Initial Demonstration of Capability (IDOC). Before reporting any data, an analyst must have on file with the QA office information demonstrating proficiency with the method. Both precision and accuracy are measured. Make four replicate analyses of the LCS at a concentration of ~ 150 to 200 µg NaCl/sample. Refer to **Step 2.** for preparation of spiking solution and spikes. Calculate the average (X) and the standard deviation (s), and compare this information to the laboratory-established criteria of 50 – 150% for accuracy and ≤ 30% RSD for precision. Where historical LCS/LCSD recovery and RSD Limits are established, use the historical limits to demonstrate proficiency.

12.2.1 If an analyst performs the desorption efficiency series of spikes, that analyst does not need to perform the IDOC in addition to the DE study. The DE study satisfies the IDOC.

12.2.2 An analyst also must be "authorized" to perform the analysis per AIHA. The approval is documented using the "Demonstration of Capability Authorization/Certification Statement", form PX-QAD-005. This document must be in the analyst's training file before they can analyze industrial hygiene samples. Reporting Level Verification.

12.3 Reporting Level/Method Detection Limit Verification (RLV/MDLV)

12.3.1 The Reporting Level must be established which is done by fortifying a media spike at a concentration at, or below the expected reporting level, which is typically equal to the lowest standard concentration. Perform all calculations defined in the method and report the concentration values in the appropriate units. The reporting level should be verified initially, annually, or if there is a significant change in the background or instrument response.

12.3.2 The percent recovery for the reporting level verification spike should be within 50-150% of the expected value. If the percent recovery is outside this range, then an additional spike should be prepared at a higher level, which will result in a higher reporting level.

12.4 Ongoing Demonstration of Capability: Every six months an analyst must demonstrate ongoing proficiency. This can be accomplished through: a) acceptable analysis of a Performance Testing (PT) sample; b) by acceptable analysis of at least 2 pairs of LCS/LCSD that were analyzed during the six month period; or c) by repeating the IDOC as described in this SOP.

12.4.1 Annually an analyst must demonstrate ongoing proficiency. This can be accomplished through: a) acceptable analysis of a Performance Testing (PT) sample; b) by acceptable analysis of at least 2 pairs of LCS/LCSD that were analyzed during the year; or c) by repeating the IDOC as described in this SOP (generally at the LCS level). Calculate the average (\bar{X}) and standard deviation (s). Where the LCS/LCSD replicates are utilized for IDOC evaluation, those same pass/fail control limits will demonstrate accuracy and precision capability.

12.4.2 The acceptable demonstration for “b” or “c” is by acceptably performing and documenting the data of four LCS (normally defined as two LCS/LCSD (BS/BSD) sets), its approval by the respective department manager, and by approval of the QA Department. Acceptable demonstration is added to the analyst’s training file.

12.4.3 Another “Demonstration of Capability Authorization/Certification Statement” must also be completed.

12.5 Control Limits

12.5.1 Once control limits have been established (in-house or by method), they are verified, reviewed, and updated if necessary on an annual basis unless the method or regulatory authority requires more frequent updating. Control limits are established per method (as opposed to per instrument) regardless of the number of instruments utilized.

12.5.2 More information concerning Control Limits can be found in Section 24.6 of the QA Manual.

12.6 Measurement Uncertainty

12.6.1 Uncertainty is “a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the

measurand" (as defined by the International Vocabulary of Basic and General Terms in Metrology, ISO Geneva, 1993, ISBN 92-67-10175-1). The minimum uncertainty associated with results generated by the laboratory can be determined by using the Laboratory Control Sample (LCS) accuracy range for a given analyte. The LCS limits are used to assess the performance of the measurement system since they take into consideration all of the laboratory variables associated with a given test over time (except for variability associated with the sampling and the variability due to matrix effects). The percent recovery of the LCS is compared either to the method-required LCS accuracy limits or to the statistical, historical, in-house LCS accuracy limits.

12.6.2 To calculate the uncertainty for the specific result reported, multiply the result by the decimal of the lower end of the LCS range percent value for the lower end of the uncertainty range, and multiply the result by the decimal of the upper end of the LCS range percent value for the upper end of the uncertainty range. These calculated values represent a 99%-certain range for the reported result. As an example, suppose that the result reported is 1.0 mg/l, and the LCS percent recovery range is 50 to 150%. The uncertainty range would be 0.5 to 1.5 mg/l, which could also be written as 1.0 +/- 0.5 mg/L.

12.6.3 Refer to the Quality Assurance Manual, Section 19.12 for further discussion of uncertainty.

12.7 Internal Quality Control Procedures. As part of the quality assurance program, the laboratory shall adhere to all stated QA/QC requirements in this SOP. Any deviations shall be documented. Deviations that result in nonconforming work shall be evaluated. The following QC checks will be performed per batch of samples:

12.7.1 Accuracy and bias. Accuracy studies are performed to determine how close a measurement comes to an actual or a theoretical value. Accuracy can be expressed as percent recovery and evaluated by analysis of laboratory control samples (LCS). Bias is a systematic error manifested as a consistent positive or negative deviation from the true value. The bias is listed in the NIOSH methods.

12.7.2 Precision. Precision is evaluated by the reproducibility of analyses and it is commonly expressed as a relative percent difference. It can be evaluated by the analysis of laboratory control sample and laboratory control samples duplicate (LCS/LCSD).

12.7.3 Blank sampling media is analyzed with each batch of samples and should be supplied by the client along with the samples. At least one field blank should be used for each day of field sampling, shipped and analyzed with each group of samples. The field blank is treated the same as the samples.

13.0 Pollution Control

13.1 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 Section 13 – Waste Management and Pollution Prevention of the Corporate Environmental Health and Safety Manual (CW-E-M-001) or the current Waste Management SOP. The following waste streams are produced when this method is carried out.

14.2 Waste Streams

14.2.1 Contaminated solid material utilized for sample preparation (i.e. contaminated filter and filter residue): If the solid material is estimated to contain <5% of the original material, they can be disposed of in the trash, unless they exhibit RCRA characteristics such as ignitability, reactivity, corrosivity or toxicity.

14.2.2 Expired primary and working standards

- I. Low concentration: Dispose of down the drain.
- II. High concentration: Dispose of down the drain.

15.0 References / Cross-References

15.1 NIOSH Method 0500, Issue 2, dated 15 August 1994.

15.2 NIOSH Method 0600, Issue 3, dated 15 January 1998.

15.3 NIOSH Method 5000, Issue 2, dated 15 August 1994.

15.4 Sartorius Balance Manual for Model CP225D.

15.5 TestAmerica Laboratories, Inc., Environmental Health and Safety Manual, CW-E-M-001.

15.6 TestAmerica – Phoenix

- Quality Assurance Manual, PX-QAD-011.
- SOP PE-SFT-001 Sample Disposal and Waste Management.
- SOP PE-QAD-008 Personnel Certification and Training.
- SOP PE-QAD-016 Balance Calibration Care and Use

15.7 AIHA Policies for Laboratory Quality Assurance Programs, May 1, 2009.

16.0 Method Modifications:

Item	Method	Modification
1	NIOSH 0500, 0600 and 5000	<i>The validated methods have been modified to use an analytical balance with readability of 0.01 mg instead of 0.001 mg.</i>

17.0 Attachments

Attachment 1: Analytical Data Review Checklist

Attachment 2: Pre-Weight and Calibration Sheet

Attachment 3: Post-Weight and Calibration Sheet

18.0 Revision History

Revision 0, dated April 2, 2008

- Integration of TestAmerica and STL operations.

Revision 1, dated August 27, 2010

- Conversion to the TestAmerica Laboratories, Inc. SOP template.

**ATTACHMENT 1
ANALYTICAL DATA REVIEW CHECKLIST
NIOSH 0500, 0600, AND 5000 METHODS**

ANALYSIS DATE: _____

MEETS CRITERIA?

- | | |
|--|-------|
| 1. INTERNAL CALIBRATION PERFORMED | Y / N |
| 2. EXTERNAL CALIBRATION CHECKS PERFORMED | Y / N |
| - 100 MG WEIGHT WITHIN $\pm 1\%$ ACCURACY | Y / N |
| - 10 MG WEIGHT WITHIN $\pm 1\%$ ACCURACY | Y / N |
| - 1 MG WEIGHT WITHIN $\pm 1\%$ ACCURACY | Y / N |
| 3. CONTINUING CALIBRATION CHECK (every 60 weight readings and at end of run) | Y / N |
| - 1 MG WEIGHT WITHIN $\pm 1\%$ ACCURACY | Y / N |
| 4. LCS/LCSD PREPARED AND ANALYZED WITH EACH BATCH | |
| -ONE PAIR PER BATCH AT $\sim 150 - 200 \mu\text{g NaCl}$ | Y / N |
| -RECOVERIES $50 - 150\%$ AND $\leq 50\%$ RPD UNTIL HISTORICAL LIMITS ARE ESTABLISHED | Y / N |
| 5. METHOD BLANK (ONE PER BATCH OF SAMPLES) | Y / N |
| - < REPORTING LEVEL | Y / N |
| 6. REPORTING LEVEL CHECK WITH EACH BATCH | |
| -ONE PER BATCH AT $\sim 100 \mu\text{g NaCl}$ | Y / N |
| -RECOVERY $50 - 150\%$ | Y / N |

COMMENTS:

ANALYST: _____ DATE: _____

REVIEWER: _____ DATE: _____

**Title: IH Air Monitoring Method for Polychlorobiphenyls
[Method No(s). NIOSH 5503]**

Approvals (Signature/Date):



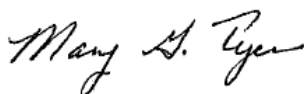
1/25/2011

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Date
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1/24/2011

Lisa Maycock
Date
Environmental Health & Safety Coordinator



1/25/2011

Mary Tyer
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Quality Assurance Manager



1/24/2011

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Date
Interim Laboratory Director

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1.0 Scope and Application

- 1.1 This method is used for the determination of Polychlorobiphenyls (PCBs) in Air using NIOSH 5503.
- 1.2 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 This standard operating procedure (SOP) is appropriate for the analysis of PCBs, such as Aroclors, on 13-mm glass fiber filters in series with 150-mg Florisil tubes. The appropriate sampling information for each chemical of interest is displayed in **Attachment 1**.
- 2.2 The NIOSH method has been modified for use with a different analytical column and different instrument parameters.

3.0 Definitions

- 3.1 Calibration Standard (CAL) – A solution prepared from the primary dilution standard solution(s) or stock standard solutions. Used to calibrate the instrument.
- 3.2 Initial Calibration Standards (ICAL) – A series of CAL solutions used to initially establish instrument calibration and develop calibration curves.
- 3.3 Continuing Calibration Verification Standard (CCV) – A CAL solution which is analyzed after every tenth field sample analysis, not including QC samples, which verifies the previously established calibration curve and confirms accurate analyte quantitation for the previous field samples analyzed. The CCV is at the highest calibration curve point concentration and may be from the same source as the calibration standards.
- 3.4 Initial Calibration Verification (ICV) – A solution, which is analyzed after the initial standards and/or at the beginning of an analysis that is at the reporting limit concentration. A standard solution (or set of solutions) used to verify calibration standard levels. The ICV shall be prepared independently from the calibration standards (from a stock solution having a different manufacturer or different manufacturer's lot identification or as an independent preparation from a neat material).
- 3.5 Laboratory Control Spike and Duplicate (LCS/LCSD) – Sorbent or media, to which a known quantity of analyte is added in the laboratory. The LCS and LCSD are analyzed exactly like the sample. LCS: A matrix-based reference material with an established concentration obtained from a source independent of the instrument calibration and traceable to NIST or other similar references materials. The LCS/LCSD is carried through the entire procedure from sample preparation through analysis as if it were a field sample. The purpose of the LCS/LCSD is the evaluate bias of the method.

- 3.6** Calibration Blank/Continuing Calibration Blank (CB/CCB) – A calibration blank and continuing calibration blank are zero concentration standards. They are in essence the solvent/reagent solution (without analyte) in which instrument calibration standards are prepared. The calibration blank and continuing calibration blank are not subject to all of the handling steps applied to samples.
- 3.7** Method Blank (MBLK) – Sorbent or media, that is treated exactly as a sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with other samples.
- 3.8** Independently Prepared Calibration Standard – A standard prepared from a reference material other than that used for calibration. When using neat materials this may be a standard prepared from the same starting material but using a different dilution technique or from a stock solution having a different manufacturer or different manufacturer's lot identification.
- 3.9** Refer to the Quality Assurance Manual for additional definitions and terms not defined in this section.

4.0 Interferences

- 4.1** Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it may need to be followed by the analysis of solvent to check for cross-contamination.

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 PPE requirement.

5.1 Specific Safety Concerns or Requirements

- 5.1.1** 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.
- 5.1.2** 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.

- 5.1.3 Use caution when scoring the glass end of the tube. Protect hand from cuts by using safe glass cutting techniques.
- 5.1.4 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: PCBs. Pure standard materials and stock standard solutions of these compounds must be handled in a hood.
- I. Additional information about the above listed analytes and all other compounds analyzed by this method is available via a MSDS. All MSDSs are available on the company's intranet site OASIS

5.2 Primary Materials Used

- 5.2.1 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	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
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.

1 – Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

- Hewlett Packard 5890 Series II / Agilent 6890 Gas chromatograph with dual electron capture detectors (ECD) – An analytical system complete with a temperature-programmable gas chromatograph suitable for split / splitless injection and all required accessories, including syringes, analytical columns and gases. The capillary column should be directly coupled to the source.
- Dual analytical columns; Primary Column – DB-608, 30-m x 0.32-mm ID x 0.5-µm film thickness fused-silica capillary column. Secondary Column – DB-5, 30-m x 0.32-mm ID x 0.25-µm film thickness fused-silica capillary column.
- Hewlett Packard Chem Station.

6.2 Supplies

- Syringes, various sizes.
- Pipettes, various sizes
- 8-mL and 12-mL glass vials and caps.
- Gas-tight syringes.
- Vortex unit or mechanical shaker.

- 150-mg Florisil tube, SKC 3226-39, or equivalent.
- 13-mm Glass Fiber Filter available from SKC, Zeflon, etc.
- Swinnex filter cassettes available from SKC, (catalog #225-32), or equivalent.
- Autosampler vials, caps and inserts.
- Tygon tubing, various sizes.

7.0 Reagents and Standards

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit use without lessening the accuracy of determination.

7.2 Life of Standards and Reagents: Reference the current version of SOP PE-QAD-013.

7.3 Hexane, pesticide residue analysis grade or equivalent.

Storage Requirements: Flammables cabinet.

7.4 PCB Stock Standards

Storage Requirements: Store the stock standard in Teflon-sealed screw-cap bottles at 0 – 6°C and protect from light.

7.5 Second source reagents of high purity should be obtained and analyzed to verify each primary source, if available.

7.6 Certificates of Analysis should be obtained for every standard.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Active Sampling with the 13-mm glass fiber filters in series with 150-mg Florisil Tubes.

8.1.1 Calibrate each personal sampling pump with a representative sampler in line.

8.1.2 Break the ends of the sampler immediately before sampling. Use a carbide blade or a metal file to score the glass ends of the tube. Place the read caps on the tube and snap off the tube ends. Keep the red caps in order to cap the tubes after sampling is finished. Attach sampler to personal sampling pump with flexible tubing. Connect the tube to the Swinnex filter cassette using the short piece of tubing. Air should be drawn into the cassette first and then through the tube.

8.1.3 Sample at an accurately known flow rate for an appropriate total sample size. Refer to **Attachment 1** in this SOP or to NIOSH 5503 for exact sampling parameters (flow rates,

duration of sampling, humidity, temperature concerns, etc.). After sampling the filter should be removed from the cassette and placed in a vial.

8.1.4 Samples should be stored cold, and shipped overnight if possible. Upon sample receipt by the laboratory, samples will be stored at a refrigerated temperature of 2° - 6° C prior to extraction.

8.1.5 The samples are stable for at least 60 days.

8.2 Field Blanks. Clients should include at least one field blank with each sample set.

9.0 Quality Control

QC Performed	Frequency	Acceptance Criteria	Correction Action
Minimum of 3 Point Calibration Curve	When an opening or continuous CCV fails.	Correlation coefficient $r^2 \geq 0.990$	1. Re-inject curve 2. Prepare new standards 3. Perform maintenance, if needed.
Primary Source CCV at Highest Calibration Concentration:	Every 10 samples and at the end of the analysis.	Within 75 – 125% of expected value	1. Re-inject CCV 2. Re-inject curve 3. Prepare new standards 4. Run new curve 5. Perform maintenance, if needed.
Independently Prepared or Second Source ICV at Reporting Level	Immediately following calibration standards and also at beginning of analysis if re-calibration is not being performed	Within 50 – 150% of expected value	1. Re-inject ICV 2. Re-inject curve 3. Prepare new standards 4. Run new curve 5. Perform maintenance, if needed.
Method Blank	One per batch of samples	< Report Limit is preferable	1. Subtract blank from client and QC samples
LCS/LCSD (Independently Prepared or Second Source) 1. Duplicate spikes near RL	Every batch of samples	Within 75 – 125% recovery or historical and $\leq 30\%$ RPD	1. Re-inject LCS/LCSD and/or qualify and report 2. Perform maintenance, if needed.
Calibration Blank	Beginning, every 10 samples, and end of each analysis day, before or after ICV	< Report Limit is expected	1) Subtract, if necessary and/or qualify and report 2) Recalibrate and reanalyze all samples since last compliant calibration blank, if needed.

9.1 It is the responsibility of the analyst to perform the analysis according to this SOP and complete the documentation required for review.

9.1.1 Personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method perform extraction and preparation of extracts.

9.2 Document all maintenance procedures in the instrument logbook assigned to each instrument.

9.3 **Method Blank and Calibration Blank**

9.3.1 A method blank must be analyzed with each batch of samples.

9.3.2 Most analytes found in the method blank will generally be below the reporting levels. However, if there is a value above the reporting level, then subtract the blank from the QC samples and the client's samples. If the method blank yields a result above the reporting level, but the client's samples do not show a background or the QC samples do not have an unusually high recovery, then the contamination is most likely isolated to that blank and further investigation should occur and an appropriate decision be made after further investigation. An appropriate decision may include, but not be limited to, re-analyzing the blank, extracting one or two additional blanks, analyzing an additional aliquot of the solvent used for extraction to check for contamination, ignoring the blank if it is obviously the only sample contaminated, etc.

9.3.3 A calibration blank is used in establishing the analytical curve and to determine background levels of the solvents/reagents. Beginning, every 10 samples, and end of each analysis day, before or after ICV.

10.0 **Procedure**

10.1 **Sample Preparation**

10.1.1 Filter and Tube sample preparation.

10.1.2 The filter portion of the sample should arrive at the laboratory in a vial. If it arrived in the Swinnex cassette, then document it in the Extraction log, and transfer the filter to a vial. Swinnex cassettes can be rinsed with hexane, dried, and used again. Prepare another vial to hold the contents of the back tube section. The front section of the tube will be transferred to the same vial containing the filter, therefore the filter/tube combo will have two vials total, and both will be analyzed.

10.1.3 Remove the glass wool from the tube and pour the contents of each section of each tube into the appropriately labeled vials.

10.1.4 Slowly add 2 mL of hexane into each vial and cap them.

10.1.5 Allow samples to stand 30 minutes with occasional agitation. The occasional agitation can be accomplished by shaking by hand for ~5 seconds every 10 to 15 minutes during 30-minute desorption procedure.

10.1.6 Immediately following the desorption process, transfer some of the extract into an autosample vial containing an insert, and then transfer the rest of the extract to a separate autosampler vial. The separate autosampler vial should be stored in the freezer in case the samples need to be re-analyzed.

10.1.7 Dilutions – If the response for any peak exceeds the calibration range, make the appropriate dilution and reanalyze.

10.1.8 Spike Solution Preparation.

- I. The spiking solution is exactly the same concentration as Intermediate #1 in the standard preparation table. A second source standard at this same concentration should be used to perform low-level spiking.

Therefore, 2 µL of spiking solution injected into Florisil in a vial would yield a spike of ~ 2 times the expected reporting level.

10.1.9 In addition to spiking the sorbent, it is often advantageous to spike a 20 mL aliquot of fresh desorption solvent with the same spike stock that was used to spike the sorbent. By doing this, the spiked solution can be used as a “reference” that tests the accuracy of the spike stock itself and the actual spiking technique, however, at this time, references are not required.

10.2 Calibration

10.2.1 According to the AIHA Policies manual, a minimum of 3 calibration standards need to be analyzed to establish a new calibration curve. A calibration blank must also be analyzed with each analysis.

10.2.2 There are several primary sources available, depending on which PCBs are of interest. Generally, a primary source will contain 1 or 2 PCBs at 1000 µg/mL each. Calibrate with the PCB of interest, if known. Default to calibrating using PCB 1242, if no PCB of interest is provided by the client. For this standard preparation example, PCB 1242 will be shown using a primary source containing PCB 1242 (µg/2 mL = µg/sample). Pattern recognition of other PCBs not used for calibration are also run at the reporting level concentration. Should a hit of a PCB other than the calibrated PCB be present, the highest calibration standard will be run and utilized for a one-point calibration curve. This will be applied toward the sample hit in question, and used to quantify the targeted PCB.

Standard ID	Preparation of Standard	PCBs 1242 (µg/mL)
Intermediate #1	100 µL of Primary source + 900 µL of hexane	100
Intermediate #2	100 µL of “Intermediate #1” + 900 µL of hexane	10
#1	200 µL of “Intermediate #2” + 800 µL of hexane	2
#2	100 µL of “Intermediate #2” into 900 µL desorption solvent	1

#3	50 µL of "Intermediate #2" into 950 µL desorption solvent	0.5
#1 x 10	100 µL of "#1" into 900 µL desorption solvent	0.2
#2 x 10	100 µL of "#2" into 900 µL desorption solvent	0.1
#3 x 10	100 µL of "#3" into 900 µL desorption solvent	0.05

10.2.3 An independently prepared standard (i.e. prepared independently from the calibration standards from neat materials or prepared with a standard from a stock solution having a different manufacturer's lot identification) should be made at the same concentration as the reporting level and/or lowest point of the calibration curve and should be within \pm 50% of the expected value. This standard is used as the ICV.

10.3 Sample Analysis

10.3.1 Analytical Conditions (may be modified, if necessary).

Hewlett Packard 5890 Series II Gas chromatograph with dual electron capture detectors (EDD)

Detector Temperatures:	320°C
Injection Port Temperature:	220°C
Oven Temperature:	140°C for 0.5 minutes, 5 °C/minute to 275 °C (hold 1 min) then 12.5 °C/minute to 300 °C (hold 11.5 min).
Run Time:	42 minutes
Injection Volume:	2 µL
Carrier Gas:	Helium
Pressure:	~11.5 psi
Splitless Injection:	Purge on at 0.5 minutes, off at 0.0 minutes

Agilent 6890 Gas chromatograph with dual electron capture detectors (ECD)

Detector Temperatures:	320°C
Injection Port Temperature:	220°C
Oven Temperature:	140°C for 0.5 minutes, 6 °C/minute to 275 °C (hold 2.5 min) then 10 °C/minute to 300 °C (hold 8.0 min).
Run Time:	36 minutes
Injection Volume:	2 µL
Carrier Gas:	Helium
Pressure:	~16 psi
Splitless Injection:	Purge on at 0.7minutes, off at 0.0 minutes, flow 50 mL/min

10.3.2

Quantitation & Confirmation
1. Calibration Blank
2. Calibration curve and/or ICV
3. Reporting Level Spikes - PCBs other than the one used for calibration
4. Calibration Blank
5. Method Blank back section
6. Method Blank front section
7. LCS
8. LCSD
9. Calibration Blank
10. Sample back sections 1 - 10
21. CCV
22. Calibration Blank
23. Sample front sections 1 – 10 (filter + front of tube)
34. CCV
35. Calibration Blank

10.4 Figure 1 and Figure 2 contain representative chromatograms of a standard and low spike containing the compounds listed in this SOP.

10.5 An instrument that continually fails to properly perform is tagged with an “out of service” label until it has been serviced or maintenance is performed such that its proper function has been restored.

11.0 Calculations / Data Reduction

11.1 Reporting Results

11.1.1 Glass Fiber Filters and Florisil Tubes.

- I. Report the blank sorbent results as the method blank results.
- II. Subtract the applicable method blank sections from the QC and the client’s samples.

11.1.2 Results for samples and all QC samples are reported to a minimum of two significant figures.

11.1.3 Data Review Checklist, **see Attachment 2.**

11.1.4 A comment is included on the certification summary page of the client’s report that the results were blank corrected. Samples and QC must be flagged if not blank corrected.

11.1.5 Quantify PCB mixtures by comparison of the retention times, peak height, and/or peak area of 5 GC peaks with the corresponding peaks in the best-matching standard. If knowledge of the PCB of interest is not provided by the client or the analyst is not able to

discern the PCB present, use PCB 1242 for reporting early eluting PCBs and either PCB 1254 or PCB 1260 as appropriate for reporting late eluting PCBs.

- 11.1.6 Any manual integrations must be performed and documented in accordance with PE-QAD-009, Manual Integration/Data Integrity.

11.2 Data Qualifiers

- 11.2.1 Use data qualifiers to qualify analytical results as needed to represent events that occurred during analysis that do not conform to SOP or Method criteria.
- 11.2.2 Refer to SOP PE-QAD-018, Use of Data Qualifiers for the proper qualifiers to use and the procedure for completing the required Corrective Action Report.

11.3 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

11.4 Precision (RPD)

$$\text{Relative Percent Difference (RPD)} = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

- 11.5 Filter/Tube Samples: Determine the mass, μg (corrected for desorption efficiency) of each analyte found in the filter/tube sample front (W_f) and tube back (W_b) sorbent sections and the media blank sorbent sections. All calculations and desorption efficiency corrections are performed by the laboratory information management system.

$$\mu\text{g/sample} = (W_f - B_f) + W_b - B_b$$

Where,

W_f = μg (corrected for desorption efficiency) front sorbent section
 W_b = μg (corrected for desorption efficiency) back sorbent section
 B_f = Media blank result front section
 B_b = Media blank result back section

- 11.6 Calculate the analyte air concentration as follows:

$$\text{mg/m}^3 = \frac{Ma}{R * T}$$

Where,

Ma = $\mu\text{g/sample}$
 R = flow rate
 T = # of minutes of sampling period

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

12.1.1 The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in the QA Manual. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.1.2 MDL is also sometimes referred to as Limit of Detection (LOD). (NELAC Requirement)

- I. "The validity of the LOD shall be confirmed by qualitative identification of the analyte(s) in a QC sample in each quality system matrix containing the analyte at no more than 2 – 3X the LOD for single analyte tests and 1 – 4X the LOD for multiple analyte tests. The verification must be performed on every instrument that is to be used for analysis of samples and reporting of data." (2003 NELAC Standards, C.3.1.b)

12.1.3 An important characteristic of expression of sensitivity is the difference in the MDL (LOD) and the Quantitation Limit or Reporting Limit (sometimes referred to as the Limit of Quantitation (LOQ)). (NELAC Requirement)

- I. "The validity of the LOQ shall be confirmed by successful analysis of a QC sample containing the analytes of concern in each quality system matrix 1 – 2 times the claimed LOQ. A successful analysis is one where the recovery of each analyte is within the established test method acceptance criteria or client data quality objective for accuracy. This single analysis is not required if the bias and precision of the measurement system is evaluated at the LOQ." (2003 NELAC Standards, C.3.2.c)

12.1.4 Additional information can be found in the QA Manual.

12.2 Initial Desorption Efficiency/Validation Study

12.2.1 Prior to ever analyzing a sample for a specific analyte, the DE for each analyte must be determined within the reporting range.

12.2.2 To perform the initial DE study, prepare and analyze 3 replicates at a concentration at the expected reporting level, 3 replicates at a mid-level and 3 replicates at the highest level. Prepare three (3) media blanks to be analyzed with the DE spikes.

12.2.3 Desorb the spikes and analyze together with calibration standards.

12.2.4 Desorption efficiency is the ratio of the amount of the analyte recovered (µg) to the amount of the analyte injected (µg). The initial DE and future % recoveries should be control charted to track historical recoveries. Once enough historical data is generated, then acceptance criteria and acceptable ranges can be updated and perhaps tightened,

if appropriate. In general, the largest variation occurs at the low end of the calibration range for spikes that are made near the reporting level.

12.3 Reporting Level Verification

- 12.3.1 The reporting level must be established. This is accomplished by fortifying a media spike at a concentration at, or below, the expected reporting level, which is typically equal to the lowest standard concentration. Perform all calculations defined in the method and report the concentration values in the appropriate units.
- 12.3.2 The reporting level media spike should be verified initially, annually, or if there is a significant change in the background or instrument response.
- 12.3.3 Percent recovery for the reporting level verification spike should be within 50 – 150% of the expected value. If the percent recovery is outside this range, then an additional spike should be prepared at a higher level, which will result in a higher reporting level.

12.4 Training Requirements

- 12.4.1 Refer to the QA Manual or to SOP PE-QAD-008 – Personnel Certification and Training. At a minimum before an analyst can perform the method independently, they must have:
 - a. Read the analytical method(s);
 - b. Read the applicable SOP(s); and
 - c. Acceptably performed and documented the data for four LCS' (normally two LCS/LCSD (BS/BSD) sets).
- 12.4.2 TestAmerica's participation in the American Industrial Hygiene Association program requires the additional performance as listed in section 12.5 – "Demonstration of Capabilities".
- 12.4.3 Additionally, training must be documented to include a description of the training content/activities and duration of the program provided to the analyst. The training course must last a minimum of 20 business days per the AIHA requirements. No independent work may be done prior to the completion of the training program.

12.5 Demonstration of Capabilities

- 12.5.1 Refer to the QA Manual for general procedures and any specific concentrations that must be used.
- 12.5.2 A Demonstration of Capability form shall be completed every six months per AIHA.
- 12.5.3 **Initial Demonstration of Capability (IDOC)**: Prior to reporting any data, each analyst must have on file with the QA office information demonstrating proficiency with the analysis technique. Both precision and accuracy are measured for the target analytes. Make four replicate analyses of a daily working standard having a concentration between 2 – 5 times the RL for each analyte (generally at the LCS level). Calculate the average (X) and standard deviation (s). Where the LCS/LCSD replicates are utilized for

IDOC evaluation, those same pass/fail control limits will demonstrate accuracy and precision capability.

- I. If an analyst performs the desorption efficiency series of spikes, that analyst does not need to perform the IDOC in addition to the DE study. The DE study satisfies the IDOC.
- II. An analyst also must be “authorized” to perform the analysis per AIHA. The approval is documented using the “Demonstration of Capability Authorization/Certification Statement”, form PX-QAD-005. This document must be in the analyst’s training file before they can analyze industrial hygiene samples.

12.5.4 Ongoing Demonstration of Capability: Every six months an analyst must demonstrate ongoing proficiency. This can be accomplished through: a) acceptable analysis of a Performance Testing (PT) sample; b) by acceptable analysis of at least 2 pairs of LCS/LCSD that were analyzed during the six month period; or c) by repeating the IDOC as described in this SOP.

- I. The acceptable demonstration for “b” or “c” is by acceptably performing and documenting the data of four LCS (normally defined as two LCS/LCSD (BS/BSD) sets), its approval by the respective department manager, and by approval of the QA Department. Acceptable demonstration is added to the analyst’s training file.
- II. Another “Demonstration of Capability Authorization/Certification Statement” must also be completed.

12.6 Control Limits (Procedure/Method Acceptance Criteria)

12.6.1 Once control limits have been established (in-house or by method), they are verified, reviewed, and updated if necessary on an annual basis unless the method or regulatory authority requires more frequent updating. Control limits are established per method (as opposed to per instrument) regardless of the number of instruments utilized.

12.6.2 More information concerning Control Limits can be found in the QA Manual.

12.6.3 Internal Quality Control Procedures. As part of the quality assurance program, the laboratory shall adhere to all stated QA/QC requirements in the method used. Any deviations from the method shall be documented. Deviations that result in nonconforming work shall be evaluated. The following QC checks will be performed per batch of samples:

12.6.4 Accuracy and bias. Accuracy studies are performed to determine how close a measurement comes to an actual or a theoretical value. Accuracy can be expressed as percent recovery and evaluated by analysis of laboratory control samples (LCS). Bias is a systematic error manifested as a consistent positive or negative deviation from the true value. The bias can be found in the original validated method by NIOSH.

- 12.6.5** Precision. Precision is evaluated by the reproducibility of analyses and it is commonly expressed as a relative percent difference. It can be evaluated by the analysis of laboratory control sample and laboratory control sample duplicate (LCS/LCSD).
- 12.6.6** Blank sampling media and analytical reagents will be analyzed with each batch of samples. At least one field blank should be used for each day of field sampling, shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the tube.
- 12.6.7** Reporting Field Blanks. The final report shall state the measured quantitative result of the field blanks submitted to the laboratory. Also, the laboratory should disclose whether or not the sample results have been corrected for contamination based on the field blank or other analytical blank.

12.7 Measurement Uncertainty (NELAC/AIHA Requirement)

- 12.7.1** Uncertainty is “a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurement” (as defined by the International Vocabulary of Basic and General Terms in Metrology, ISO Geneva, 1993, ISBN 92-67-10175-1). The minimum uncertainty associated with results generated by the laboratory can be determined by using the Laboratory Control Sample (LCS) accuracy range for a given analyte. The LCS limits are used to assess the performance of the measurement system since they take into consideration all of the laboratory variables associated with a given test over time (except for variability associated with the sampling and the variability due to matrix effects). The percent recovery of the LCS is compared either to the method-required LCS accuracy limits or to the statistical, historical, in-house LCS accuracy limits.
- 12.7.2** To calculate the uncertainty for the specific result reported, multiply the result by the decimal of the lower end of the LCS range percent value for the lower end of the uncertainty range, and multiply the result by the decimal of the upper end of the LCS range percent value for the upper end of the uncertainty range. These calculated values represent a 99%-certain range for the reported result. As an example, suppose that the result reported is 1.0 mg/l, and the LCS percent recovery range is 50 to 150%. The uncertainty range would be 0.5 to 1.5 mg/l, which could also be written as 1.0 ± 0.5 mg/L.
- 12.7.3** Refer to the Quality Assurance Manual for further discussion of uncertainty.

13.0 Pollution Control

- 13.1.1** 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 Section 13 – Waste Management and Pollution Prevention of the Corporate Environmental Health and Safety Manual (CW-E-M-001) or the current Waste Management SOP. The following waste streams are produced when this method is carried out.

14.2 Waste Streams:

14.2.1 Autosampler vial waste (Open Top Metal Drum): The used vials will be collected and stored in labeled containers located in the fume hood cabinets. When the containers are full, they will be transported in the same container to the storage area. The vials will then be safely and gently transferred to the drum, via a funnel to minimize fumes during removal of the drum lid, ensuring no vial breakage.

14.2.2 Mixed solvent waste (Closed Top Metal Drum): Solvent waste is stored in appropriately labeled hazardous waste containers in satellite storage areas throughout the lab, and should be emptied as often as possible. The waste should be transferred to the storage area in these exact same containers. The snorkel valve on the fume hood exhaust tubing should be turned 90 degrees clockwise to direct flow to the snorkel. The drum openings should then be opened with a wrench. The carboy placed over one opening and the snorkel placed over the other opening. The valve for the carboy should then be opened thereby transferring the contents of the carboy into the waste drum.

14.2.3 Expired primary and working standards:

- I. Low concentration (<1000 PPM): Dispose of in the solvent waste stream.
 - a. If the standard is prepared in water, dispose in the acidic waste stream.
- II. High concentration: (>1000 PPM) Lab pack.
- III. Dioxin Precursors (>50 PPM). Lab Pack
 1. PCBs

14.3 Any waste, which does not fit into any of the waste streams or cannot be disposed of in any of the other drums, should be brought directly to the department manager's attention

15.0 References / Cross-References

15.1 Test Methods

- NIOSH 5503, Polychlorobiphenyls in Air, Issue 2, 15 August 1994.
- Method TO-10 A, Determination of Pesticides and PCBS in Ambient Air Using Low Volume PUF Sampling Followed by Gas Chromatographic/Multi-Detector (GC/MD) Detection, January 1999.

- 15.2** TestAmerica Laboratories, Inc.
- Environmental Health and Safety Manual, CW-E-M-001.
- 15.3** TestAmerica Phoenix Policies and Procedures
- TestAmerica – Phoenix, Quality Assurance Manual, PX-QAD-011.
 - SOP PE-SFT-001 - Laboratory Waste Disposal.
 - SOP PE-QAD-008 – Personnel Certification and Training.
 - PE-QAD-009 Manual Integrations
 - PE-QAD-022 Good Calibration Practices
 - PE-QAD-018 Use of Data Qualifiers
- 15.4** AIHA Policies for Laboratory Quality Assurance Programs, April 1, 2010.

16.0 Method Modifications:

Item	Method	Modification
1.	NIOSH 5503	Dual column, dual detector analysis for confirmation utilizing the following analytical columns: Dual analytical columns; Primary Column – DB-608, 30-m x 0.32-mm ID x 0.5- μ m film thickness fused-silica capillary column. Secondary Column – DB-5, 30-m x 0.32-mm ID x 0.25- μ m film thickness fused-silica capillary column. (Use of updated columns is not considered a modification to the method per AIHA.)
2.	NIOSH 5503	The desorption solvent volume has been modified from 5 mL front section; 2ml back section to 2 mL front section; 2ml back section. Desorption efficiency studies have been performed for validation.
3.	NIOSH 5503	Desorption time has been increased to 30 minutes from 20 minutes. Desorption efficiency studies have been performed for validation.

17.0 Attachments

Attachment 1: Sampling Information
Attachment 2: Analytical Data Review Checklist
Attachment 3: Figure 1 / Figure 2 Representative Chromatographs

18.0 Revision History

- Revision 0, dated April 3, 2008
- Integration of TestAmerica and STL operations.
- Revision 1, dated January 28, 2011
- Conversion to the TestAmerica Laboratories, Inc. SOP template.

Attachment 1

Sampling Information

Chemical Name	Maximum Sample Storage	OSHA PEL TWA STEL	NIOSH REL TWA STEL	ACGIH TLV TWA STEL	Sampling Rates (L/min)	Air Volume Minimum Maximum	Reporting Level (µg/sample)
Aroclor 1016	60 days	1 mg/m ³	0.001 mg/m ³	1 mg/m ³	0.05 – 0.2	1 - 50	0.1
Aroclor 1221	60 days				0.05 – 0.2	1 - 50	0.1
Aroclor 1232	60 days				0.05 – 0.2	1 - 50	0.1
Aroclor 1242	60 days	0.5 mg/m ³	0.001 mg/m ³	0.5 mg/m ³	0.05 – 0.2	1 - 50	0.1
Aroclor 1248	60 days				0.05 – 0.2	1 - 50	0.1
Aroclor 1254	60 days				0.05 – 0.2	1 - 50	0.1
Aroclor 1260	60 days				0.05 – 0.2	1 - 50	0.1
Aroclor 1268	60 days				0.05 – 0.2	1 - 50	0.1

Definitions of acronyms and abbreviations in Attachment 1:

PEL = Permissible Exposure Limit

REL = Recommended Exposure Limit

STEL = Short Term Exposure Limit (usually based on 15-minute sampling period)

TLV = Threshold Limit Value

TWA = Time-Weighted Average (usually based on 8-hour workday)

OSHA = Occupational Safety and Health Administration

NIOSH = National Institute for Occupational Safety and Health

ACGIH = American Conference of Governmental Industrial Hygienists

LFC = lowest feasible concentration

mL/min = milliliters per minute

mg/m³ = milligrams per cubic meter

Ceiling = the highest concentration allowable ever

Attachment 2

**ANALYTICAL DATA REVIEW CHECKLIST
NIOSH 5503**

Analysis Date: _____ Batch #: _____

MEETS CRITERIA?

- | | |
|---|------------------------------|
| 1. CALIBRATION CURVE (3 LEVELS MINIMUM)
-ALL TARGET COMPOUNDS ($r^2 \geq 0.990$)
-DATE OF INITIAL CALIBRATION _____ | Y / N |
| 2. OPENING ICV
[INDEPENDENTLY PREPARED OR SECOND SOURCE STANDARD]
-REPORTING LEVEL ICV ($\pm 50\%$ of target) | Y / N |
| 3. CONTINUING CALIBRATION VERIFICATION (CCV)
-CCV NEAR HIGHEST STANDARD CONC. ($\pm 25\%$ of target)
-EVERY 10 SAMPLES AND AT END OF ANALYSIS | Y / N
Y / N |
| 4. METHOD BLANK
-ANALYZE ONE PER BATCH | Y / N |
| 5. LCS/LCSD PREPARED AND ANALYZED WITH EACH BATCH
[INDEPENDENTLY PREPARED OR SECOND SOURCE STANDARD]
-ONE PAIR PER BATCH AT ~ 2-5 TIMES THE REPORTING LEVEL
- ALL RECOVERIES 75 - 125% AND $\leq 30\%$ RPD OR HISTORICAL | Y / N
Y / N |
| 6. CALIBRATION BLANK/CONTINUING CALIBRATION BLANK (CB/CCB)
- < RL
- EVERY 10 SAMPLES, ONE BEFORE/FOLLOWING OPENING CCV AND
AT END OF ANALYSIS | Y / N |

COMMENTS:

ANALYST: _____ DATE: _____

REVIEWER: _____ DATE: _____

Attachment 3

Figure 1. Representative Standard Solution Containing Aroclor 1016 and 1260.

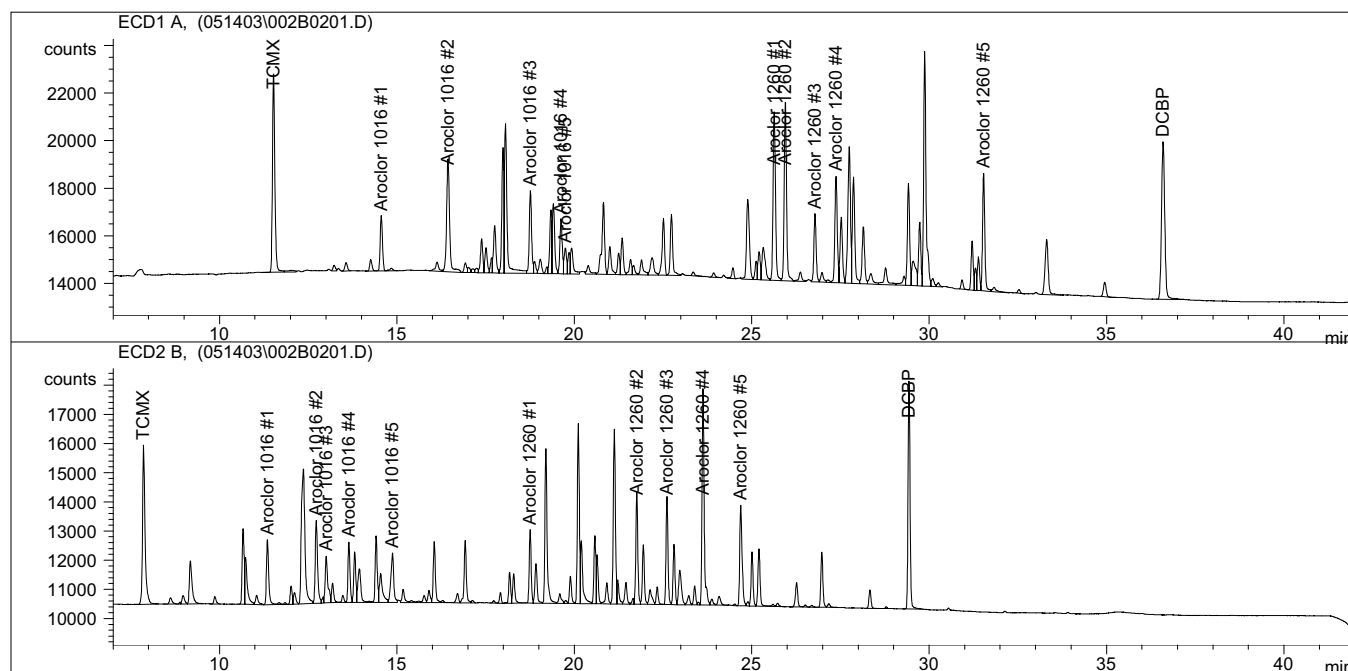
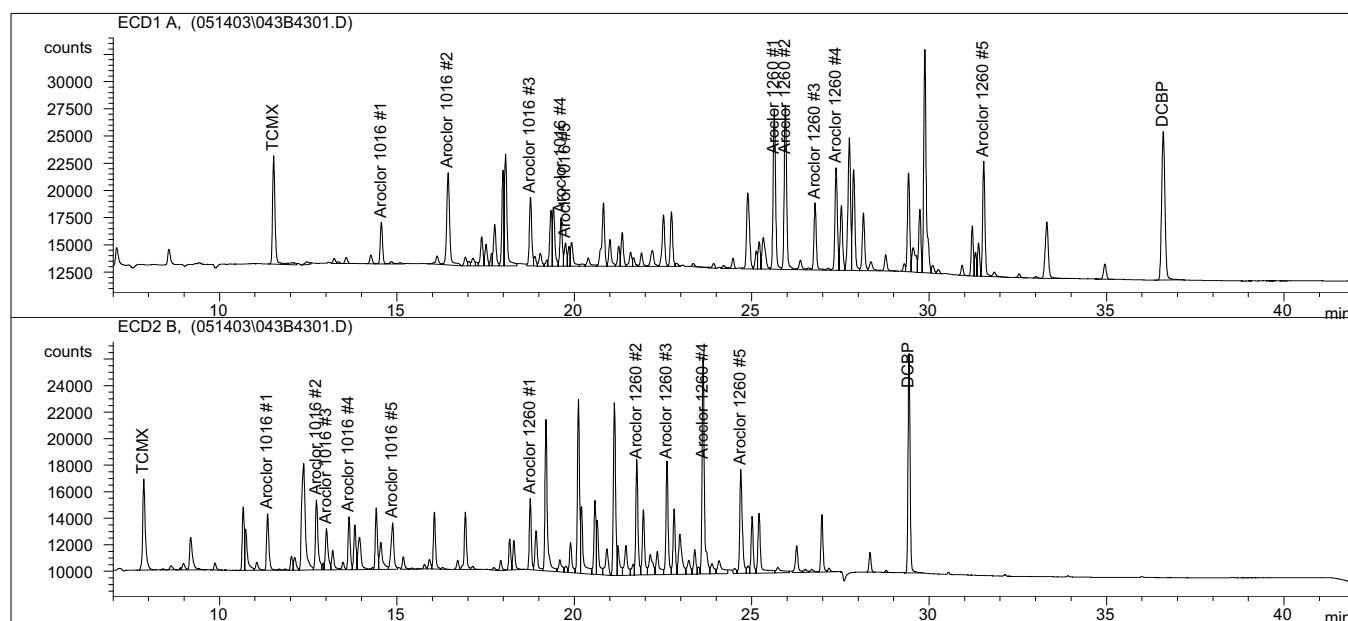


Figure 2. Representative Low Spike Containing Aroclor 1016 and 1260.



**Title: IH Air Monitoring Method for Polynuclear Aromatic
Hydrocarbons
[Method No(s). NIOSH 5506]**

Approvals (Signature/Date):



5/09/2012

Stephanie Stimson
Date
Industrial Hygiene Department Manager



5/09/2012

Lisa Maycock
Date
Environmental Health & Safety Coordinator



5/18/2012

Melissa Spencer
Date
Quality Assurance Manager



5/22/2012

Shawn Kusma
Date
Laboratory Director

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1.0 **Scope and Application**

- 1.1 This standard operating procedure (SOP) is appropriate for the analysis of polynuclear aromatic hydrocarbons (PAHs or PNAs) by modified NIOSH 5506. The following analytes can be determined by this method:

Naphthalene	Acenaphthylene
Acenaphthene	Fluorene
Phenanthrene	Antracene
Fluoranthene	Pyrene
Benzo(a)anthracene	Chrysene
Benzo(b)fluoranthene	Benzo(k)fluoranthene
Benzo(a)pyrene	Dibenzo(a,h)anthracene
Benzo(g,h,i)perylene	Indeno(1,2,3-cd)pyrene

- 1.2 The validated method has been modified to use different analytical conditions, which provide sufficient separation for all compounds listed above.
- 1.3 The reporting level (RL) for an individual compound is somewhat instrument dependent. The reporting level for each analyte is listed in Attachment 1.
- 1.4 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 PAHs listed in the SOP are sampled actively by using a personal sampling pump to pull air through a filter/tube combination consisting of a 37-mm PTFE (Teflon) filter with backup pad in a 37-mm cassette in series with a 150-mg XAD-2tube. The filter cassette is attached to the front of the tube with a Luer adapter and a very short piece of tubing. The filter is used to capture PAH aerosols (dusts, particulates, etc), whereas the tube will efficiently collect PAH vapor that passes through the filter. The filter (and backup pad) and tube contents are extracted with acetonitrile. Samples are analyzed by high performance liquid chromatography (HPLC) with an ultraviolet detector (UV) and a fluorescence detector (FLD). Attachment 1 displays the appropriate sampling and analytical information for each analyte of interest.

3.0 **Definitions**

- 3.1 Calibration Standard (CAL) – A solution prepared from the primary dilution standard solution(s) or stock standard solutions. Used to calibrate the instrument.
- 3.2 Initial Calibration Standards (ICAL) - A series of CAL solutions used to initially established instrument calibration and develop calibration curves.

- 3.3** Initial Calibration Verification (ICV) – A solution, which is analyzed after the initial standards and/or at the beginning of an analysis that is at the reporting limit concentration. A standard solution (or set of solutions) used to verify calibration standard levels. The ICV shall be prepared independently from the calibration standards (from a stock solution having a different manufacturer or different manufacturer's lot identification or as an independent preparation from a neat material). The concentration for the ICV is at or below the reporting level.
- 3.4** Continuing Calibration Verification Standard (CCV) – A CAL solution which is analyzed after every ten field sample analysis, not including QC samples, which verifies the previously established calibration curve and confirms accurate analyte quantitation for the previous field samples analyzed. The concentration for the CCV should be at the highest calibration level.
- 3.5** Laboratory Control Spike and Duplicate (LCS/LCSD) – Sorbent or media, to which a known quantity of analyte is added in the laboratory. The LCS and LCSD are analyzed exactly like the sample. LCS: A matrix-based reference material with an established concentration obtained from a source independent of the instrument calibration and traceable to NIST or other similar reference materials. The LCS/LCSD is carried through the entire procedure from sample preparation through analysis as if it were a field sample. The purpose of the LCS/LCSD is to evaluate bias of the method.
- 3.6** Calibration Blank/Continuing Calibration Blank (CB/CCB) – A calibration blank and continuing calibration blank are zero concentration standards. They are in essence the solvent/reagent solution (without analyte) in which instrument calibration standards are prepared. The calibration blank and continuing calibration blank are not subject to all of the handling steps applied to samples.
- 3.7** Method Blank (MB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with other samples.
- 3.8** Relative Percent Difference (RPD) – The difference between two values divided by the average of the values as expressed as a percent.
- 3.9** Precision – The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. It is concerned with the closeness of results.
- 3.10** Demonstration of Capability (DOC) – A procedure to establish the ability of the analyst to generate acceptable accuracy and precision.
- 3.11** Accuracy – The degree of agreement of a measured quality of concern.
- 3.12** Independently Prepared Calibration Standard – A standard prepared from a reference material other than that used for calibration. When using neat materials this may be a standard prepared from the same starting material but using a different dilution technique or from a stock solution having a different manufacturer or different manufacturer's lot identification.

- 3.13 Refer to the Quality Assurance Manual Glossary/Acronyms for additional definitions and terms not defined in this section.

4.0 **Interferences**

- 4.1 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections. Whenever an unusually concentrated sample is encountered, it might need to be followed by the analysis of solvent to check for cross-contamination.

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 following method analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: Benzo(a)anthracene, Benzo(a)pyrene, and Dibenzo(a,h)anthracene.
- I. Additional information about the above listed analytes and all other compounds analyzed by this method is available via a MSDS. All MSDSs are available on the company's intranet site OASIS.
- 5.1.3 There are areas of high voltage in the HPLC and its detectors. 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**

- 5.2.1 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 equipment 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
Acetonitrile	Flammable Poison	40 ppm-TWA	Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

- Sonication extraction apparatus.
- Supelcosil LC-PAH column, 15 cm x 4.6 mm, 5 μ m (PN# 58318) or equivalent. Phenomenex SecurityGuard cartridge system (PN# KJO-4282) or equivalent and Guard Column, C18 (ODS, Octadecyl) 4mm LX 3.0 mm ID (PN# AJO-4287) or equivalent.
- Hewlett Packard 1100 HPLC or equivalent, equipped with Diode Array detector (DAD) and Fluorescence (FLD) detector. The Diode Array Detector is a UV detector.
- Data processing station, compatible with detectors and capable of measuring peak areas, peak heights and retention times, HP Chemstation for LC.
- Column heater.
- Mobile phase reservoirs and degassing unit – for filtering/degassing HPLC mobile phase. Filtration system uses a 0.18 μ m filter.

6.2 Supplies

- Syringes – various sizes.
- Syringe Filters: 25 mm, 0.45 μ m PTFE filters.
- 8-mL and 12-mL glass vials and caps.
- Personal sampling pump, capable of flows up to 2 L/min, with flexible connecting tubing.
- 37-mm PTFE (Teflon) filters, with backup pad in 37-mm polystyrene cassettes, available from SKC, or equivalent.
- 150-mg XAD-2 tubes, available from SKC, or equivalent.
- 2-mL, screw top, HPLC autosampler vials and caps.

7.0 Reagents and Standards

7.1 E-pure reagent water delivery system or equivalent.

7.2 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of determination.

7.3 Reagent water: Reagent water is defined as water in which an interference is not observed at the reporting limit of each parameter of interest.

7.4 Acetonitrile: HPLC quality.

Life of Reagent: Reference the current version of SOP PE-QAD-013.

Storage Requirements: Flammables storage.

7.5 Standards: Stock standard solutions may be purchased as certified solution or prepared from pure materials. Purchased stock standards may be used until certified expiration dates unless performance indicates a problem.

7.6 Second source reagents of high purity should be obtained and analyzed to verify each primary source when available.

7.7 Unless otherwise noted, follow the manufacturer's expiration date. If no expiration date is provided follow the guidelines in the SOP PE-QAD-013, Reagent and Standard Preparation, Control, and Documentation.

7.8 Certificates of Analysis should be obtained for every neat or commercially prepared standard.

8.0 **Sample Collection, Preservation, Shipment and Storage**

8.1 Sampling with the Filter/Tube Combination

8.1.1 Calibrate each personal sampling pump with a representative sampler (filter/tube sampling train) in line.

8.1.2 Break the ends of the tube immediately before sampling using a tube tip breaker. Attach the back end of the tube to the personal sampling pump with the flexible tubing.

I. Attach the tube to a personal sampling pump with the flexible tubing and tube holder provided. Wrap the tube in aluminum to protect from light during sampling. Place the tube into the tube holder. Make sure the tube is facing the correct way, which is for the air to be pulled in through the front and out the back of the tube. The tube should have a small arrow on it, which indicates the direction of flow. Attach the filter cassette to the inlet of the tube using a short piece of tubing and (2) Luer adapters, making sure the outlet of the cassette is closest to the inlet of the tube. Attach a very short piece of tubing to the front end of the tube and then attach the larger end of a Luer adapter to the other end of tubing.

II. The filter/tube combination is the entire sampling train and is necessary to efficiently collect PNA aerosols and vapors that may be present.

8.1.3 Sample at an accurately known flow rate for an appropriate total sample size. Refer back to the validated method reference for exact sampling parameters such as flow rates, duration of sampling, humidity, and temperature concerns, etc.

- 8.1.4** Once sampling is complete, the tube must have plastic caps placed over each end of the tube and the filter cassette needs to be capped with the caps that were originally on it. Wrap the tube in aluminum foil to avoid degradation due to light.
- 8.1.5** Samples should be stored on blue ice and shipped over night, and once the samples are received by this facility, they should be stored at refrigerator temperatures until extracted.

9.0 Quality Control

QC Performed	Frequency	Acceptance Criteria	Corrective Action
Minimum of 3 Point Calibration Curve	When an opening or continuing CCV fails.	Correlation coefficient $r > 0.995$	1) Re-inject curve 2) Prepare new standards 3) Perform maintenance
Primary Source CCV at Highest Calibration Concentration:	Every 10 samples and at the end of the analysis.	Within 80 – 120% of expected value	1) Re-inject curve 2) Prepare new standards 3) Run new curve 4) Perform maintenance
Second Source ICV at/or Below Reporting Level	Immediately following calibration standards and also at beginning of analysis if re-calibration is not being performed.	Within 60 – 140% of expected value	1) Re-inject curve 2) Prepare new standards 3) Run new curve 4) Perform maintenance
Method Blank	One per batch of samples	< Report Limit is preferable	1) Subtract blank from client samples and QC samples
LCS/LCSD (Second Source) 1) Duplicate Tube Front Sections	Every batch of samples	Within 50 – 150% recovery or Historical $\leq 50\%$ RPD	1) Re-inject LCS/LCSD and/or qualify and report. 2) Perform maintenance
Calibration Blank	Beginning, every 10 samples, and end of each analysis day, before or after ICV	< Report Limit is expected	–1) Subtract, if necessary and/or qualify and report –2) Recalibrate and reanalyze all samples since last compliant calibration blank, if needed.

- 9.1** It is the responsibility of the analyst to perform the analysis according to this SOP and complete the documentation required for review.
- 9.1.1** Only personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method perform extraction and preparation of extracts.
- 9.2** Document all maintenance procedures in the instrument logbook assigned to each instrument.
- 9.3** Method Blank and Calibration Blank

- 9.3.1** A method blank filter and method blank tube must be analyzed with each batch of samples.
- 9.3.2** Any background contamination is the method blank will generally be below the reporting levels. However, if there is a value above the reporting level, then subtract the blank from the QC samples and the client's samples. If the method blank yields a result above the reporting level, but the client's samples do not show a background or the QC samples do not have an unusually high recovery, then the contamination is most likely isolated to that blank and further investigation should occur and an appropriate decision be made after further investigation. An appropriate decision may include, but not be limited to, re-analyzing the blank, extracting one or two additional blanks, analyzing an additional aliquot of the solvent used for extraction to check for contamination, ignoring the blank if it is obviously the only sample contaminated, etc.
- 9.3.3** A calibration blank is used in establishing the analytical curve and to determine background levels of the solvents/reagents. Beginning, every 10 samples, and end of each analysis day, before or after ICV.

10.0 Procedure

10.1 Sample Preparation

- 10.1.1** Remove the filter and backup pad from the cassette and transfer them to a vial. Discard the cassette housing.
- 10.1.2** Transfer the front glass wool plug and front sorbent section into a vial. Transfer the middle wool plug and back sorbent section into a vial.
- 10.1.3** There should be a total of 3 vials for every sample.
- 10.1.4** Add 5 mL of acetonitrile to each vial and cap each vial.
- 10.1.5** Place every capped sample vial (including spikes and blanks) into a sonic bath and sonicate the samples for 60 minutes in the warm sonic bath.
- 10.1.6** Immediately following the desorption/extraction process, filter each sample extract with a 25 mm, 0.45 μ m PTFE syringe filter. Transfer a portion of the sample extracts to autosampler vials for analysis. All sections of the sample (filter, tube front, and tube back) must be analyzed.
- 10.1.7** Dilutions – If the response for any peak exceeds the calibration range, make the appropriate dilution and reanalyze.
- 10.1.8** Spike Preparation Techniques – Examples using the second source standard.
- 10.1.9** Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD) – also referred to as laboratory spikes.

- 10.1.10** One pair of LCS/LCSD on tubes must be prepared and analyzed with each batch of samples. The LCS/LCSD should be prepared by injecting 15 μ L of secondary stock into each tube front section that are being used for spikes. The recoveries must be within $\pm 50\%$ of the expected recovery and $\leq 50\%$ RPD. The expected recovery is established from original DE studies and ongoing historical recoveries. Standard concentrations are in terms of μ g/mL, so these types of spikes are effectively being diluted by a factor of 5, because they are extracted with 5 mL instead of 1 mL.
- 10.1.11** Tube spikes – For each spike transfer the XAD-2 resin from the front section of a blank tube into an 8-mL vial and inject 15 μ L of standard onto the XAD-2 resin. Cap the vial and allow the vial to sit for ~30 minutes to let the spike dry. After the drying process is complete, add 5 mL of acetonitrile to each vial to extract the spikes.
- 10.1.12** In addition to spiking the media, it is often advantageous to spike a 5-mL aliquot of fresh desorption solvent with the same spike stock or neat analyte that was used to spike the media. By doing this, the spiked solution can be used as a “reference” that tests the accuracy of the spike stock itself and the actual spiking technique. References should be used if recovery accuracy becomes a problem, however, at this time references are not required with each analysis.

10.2 Calibration

- 10.2.1** As per the AIHA Policies manual, a minimum of 3 calibration standards need to be analyzed to establish a new calibration curve. However, this laboratory typically runs 7 calibration standards to establish a calibration curve with each analysis that requires re-calibration. An example of a 7-point calibration is shown in this SOP. Fewer standards may be used (minimum of 3) as long as the acceptance criteria are met.
- 10.2.2** PNA Stock Standards. Supelco EPA 610 PNA Mix, Cat. No. 4-8743 and Second Source EPA 610 PNA Mix, Cat. No. 4S-8743. Contains the target compounds in a range from 100 – 2000 μ g/mL.
- 10.2.3** 7-Point Calibration Curve / CCV – Example Preparation.
- 10.2.4** Curve / CCV intermediate stock, “Standard #1”. 100 μ L of the primary source PNA stock in a 1.5 mL screw cap autosampler vial containing 900 μ L of acetonitrile. Store in an autosampler vial rack. Concentrations are 10 – 200 μ g/mL for the PNAs.
- 10.2.5** Follow the dilution table below to prepare each calibration standard in screw cap autosampler vials. The dilution solvent is acetonitrile (ACN). Standard “1 x 500” should be used as the reporting level CCV. See Attachment 2 for the analyte concentrations of the highest Working Standard.

Standard #	Preparation	Concentration Range (μ g/mL)
1 x 5	200 μ L Standard #1 + 800 μ L ACN	2.0 – 40.0
1 x 10	100 μ L Standard #1 + 900 μ L ACN	1.0 – 20.0
1 x 20	50 μ L Standard #1 + 950 μ L ACN	0.5 – 10.0
1 x 50	20 μ L Standard #1 + 980 μ L ACN	0.2 – 4.0

1 x 100	10 µL Standard #1 + 990 µL ACN	0.1 – 2.0
1 x 200	50 µL “#1 x 10” + 950 µL ACN	0.05 – 1.0
1 x 500	20 µL “#1 x 10”+ 980 µL ACN	0.02 – 0.4

10.2.6 An independently prepared standard (i.e. prepared independently from the calibration standards from neat materials or prepared with a standard from a stock solution having a different manufacturer or different manufacturer’s lot identification) should be made at the same concentration as the lowest point of the calibration curve (i.e., the equivalent of Standard ID “#500”) and should be within $\pm 40\%$ of the expected value.

10.3 Sample Analysis

10.3.1 Agilent 1100 Series HPLC Instrument Conditions:

TIME (min.) INITIAL	FLOW (mL/min.)	ACETONITRILE (%)	WATER (%)
1	1.25	50	50
16 - 27	1.25	100	0
Post run - 5 minutes	1.25	50	50

UV Detector is set at 254 nm, BW 4 nm. Peakwidth > 0.1, slit is 4 nm. The Fluorescence Detector (FLD) is programmed at 265 nm for excitation, emission A – zero order, emission B – 370 nm, emission C – 445 nm, and emission D – 445 nm. FLD scan range: 220 to 380 nm, step 5 nm for excitation and 300 to 500 nm, step 5 nm for emission. Gain is 10. The FLD program and analytical conditions listed in this SOP may be adjusted as needed, but must be documented in the maintenance logbook. Column thermostat set at 28.0 °C, injection volume is 20 µL.

Quantitation & Confirmation
1. Calibration Blank
2. Calibration curve or ICV
3. Calibration Blank
4. Method Blank
5. LCS
6. LCSD
7. Calibration Blank
8. Sample particulate sections 1 - 10
19. CCV
20. Calibration Blank
21. Sample back sections 1 - 10
32. CCV
33. Calibration Blank
34. Sample front sections 1 - 10
45. CCV
46. Calibration Blank

10.3.2 Preventive Maintenance.

- I. Run 100% acetonitrile after every sequence for 20 – 30 minutes to clean up the column and the remaining water (the system is currently programmed to perform this at sequence end).
- II. Document all maintenance procedures in the instrument logbook assigned to the instrument.
- III. The system can be periodically flushed with methanol, followed by acetonitrile to clean it. Disconnect the column before performing this procedure. Make sure the methanol has cleared the system before reconnecting the column.
- IV. An instrument that continually fails to properly perform is tagged with an “out of service” label until it has been serviced or maintenance is performed such that its proper function has been restored.

10.3.3 Analytical conditions may be modified as necessary. Alternative HPLC equipment may also be used, if available. However, a DE/Validation Study must be performed on each instrument.

11.0 Calculations / Data Reduction

11.1 For sampling information on a specific analyte, see Attachment 1.

11.2 Data Review Checklist, see Attachment 3.

11.3 Results for samples and all QC samples will be reported to three significant figures.

11.4 Report compounds from the detector indicated in Attachment 3.

11.5 A comment is included on the certification summary page of the client's report that the results were blank corrected. Samples and QC must be flagged if not blank corrected.

11.6 Calculate each calibration factor (CF):

$$CF = (A_x)/(C_x)$$

Where:

A_x = Area of the compound in the standard

C_x = Concentration of the compound being measured (in $\mu\text{g/L}$)

11.7 Calculate each mean calibration factor (CF):

$$\overline{CF} = \frac{\sum CF_i}{n}$$

Where:

CF_i = Calibration factor for calibration standard (I=1-5)
η = Number of calibration standards

11.8 **Accuracy**

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

11.9 **Precision (RPD)**

$$\text{Relative Percent Difference (RPD)} = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

11.10 **Tube Samples:** Determine the mass, μg of analyte found in the tube sample front (W_f) and back (W_b) sorbent sections and the media blank sorbent sections.

$$\mu\text{g/sample} = (W_f - B_f) + (W_b - B_b) \times 5$$

Where:

W_f = μg analyte on front sorbent section
W_b = μg analyte on back sorbent section
B_f = Media blank result front section
B_b = Media blank result back section
5 = 5 mL (standard concentration and original sample result is per mL and must be converted to 5 mL total to get total μg/tube)

11.11 **Filter Samples:** Determine the mass, μg of analyte found on the sample (W_f) and the media blank.

$$\mu\text{g/sample} = (W_f \times 5) - (B_f \times 5)$$

Where:

W_f = μg front sorbent section
B_f = Media blank result front section
5 = 5 mL (standard concentration and original sample result is per mL and must be converted to 5 mL total to get total μg/sample)

11.12 The concentration of each analyte in air can be determined using the following equation:

$$\text{ppm} = \frac{\mu\text{g/sample} \times 24.45}{\text{M.W.} \times V}$$

Where:

$\mu\text{g/sample}$ = mass found on the filter + mass found on the sorbent tube
24.45 = ideal gas constant that has been corrected for standard temperature
 V = volume of air pulled through sample in liters
M.W. = molecular weight of analyte

- 11.13 All of the calculations shown here are performed manually or by the laboratory information management system (LIMS).

12.0 Method Performance

12.1 Initial Desorption Efficiency/Validation Study

- 12.1.1 Prior to ever analyzing a sample for a specific analyte, the DE for each analyte must be determined within the reporting range.
- 12.1.2 To perform the initial DE study, prepare and analyze 3 replicates at a concentration at the expected reporting level, 3 replicates at a mid-level and 3 replicates at the highest level. Prepare three (3) media blanks to be analyzed with the DE spikes.
- 12.1.3 Desorb the spikes and analyze together with calibration standards.
- 12.1.4 Desorption efficiency is the ratio of the amount of the analyte recovered (μg) to the amount of the analyte injected (μg). The initial DE and future % recoveries should be control charted to track historical recoveries. Once enough historical data is generated, then acceptance criteria and acceptable ranges can be updated and perhaps tightened, if appropriate. In general, the largest variation occurs at the low end of the calibration range for spikes that are made near the reporting level.

12.2 Reporting Level Verification

- 12.2.1 The reporting level must be established. This is accomplished by fortifying a media spike at a concentration at, or below, the expected reporting level, which is typically equal to the lowest standard concentration. Perform all calculations defined in the method and report the concentration values in the appropriate units.
- 12.2.2 The reporting level media spike should be verified initially, annually, or if there is a significant change in the background or instrument response.
- 12.2.3 Percent recovery for the reporting level verification spike should be within 50 – 150% of the expected value. If the percent recovery is outside this range, then an additional spike should be prepared at a higher level, which will result in a higher reporting level.

12.3 Training Requirements

- 12.3.1 Refer to the QA Manual or to SOP PE-QAD-008 – Personnel Certification and Training. At a minimum before an analyst can perform the method independently, they must have:

~~12.1.1a.~~ Read the analytical method(s);

- ~~12.1.2b.~~ Read the applicable SOP(s); and
- ~~12.1.3c.~~ Acceptably performed and documented the data for four LCS' (normally two LCS/LCSD (BS/BSD) sets).

12.3.2 TestAmerica's participation in the American Industrial Hygiene Association program requires the additional performance as listed in section 12.4 – "Demonstration of Capabilities".

12.3.3 Additionally, training must be documented to include a description of the training content/activities and duration of the program provided to the analyst. The training course must last a minimum of 20 business days per the AIHA requirements. No independent work may be done prior to the completion of the training program.

12.4 Demonstration of Capabilities (DOC)

12.4.1 Refer to the QA Manual for general procedures and any specific concentrations that must be used.

12.4.2 A Demonstration of Capability form shall be completed every six months per AIHA.

12.4.3 Initial Demonstration of Capability (IDOC): Prior to reporting any data, each analyst must have on file with the QA office information demonstrating proficiency with the analysis technique. Both precision and accuracy are measured for the target analytes. Make four replicate analyses of a daily working standard having a concentration between 10 – 50 times the MDL for each analyte (generally at the LCS level). Calculate the average (X) and standard deviation (s). Where the LCS/LCSD replicates are utilized for IDOC evaluation, those same pass/fail control limits will demonstrate accuracy and precision capability.

12.4.4 If an analyst performs the desorption efficiency series of spikes, that analyst does not need to perform the IDOC in addition to the DE study. The DE study satisfies the IDOC.

12.4.5 An analyst also must be "authorized" to perform the analysis per AIHA. The approval is documented using the "Demonstration of Capability Authorization/Certification Statement", form PX-QAD-005. This document must be in the analyst's training file before they can analyze industrial hygiene samples.

12.4.6 Ongoing Demonstration of Capability: Every six months an analyst must demonstrate ongoing proficiency. This can be accomplished through: a) acceptable analysis of a Performance Testing (PT) sample; b) by acceptable analysis of at least 2 pairs of LCS/LCSD that were analyzed during the six month period; or c) by repeating the IDOC as described in this SOP.

12.4.7 Annually an analyst must demonstrate ongoing proficiency. This can be accomplished through: a) acceptable analysis of a Performance Testing (PT) sample; b) by acceptable analysis of at least 2 pairs of LCS/LCSD that were analyzed during the year; or c) by repeating the IDOC as described in this SOP (generally at the LCS level). Calculate the average (X) and standard deviation (s). Where the LCS/LCSD replicates are utilized for

IDOC evaluation, those same pass/fail control limits will demonstrate accuracy and precision capability.

12.4.8 The acceptable demonstration for “b” or “c” is by acceptably performing and documenting the data of four LCS (normally defined as two LCS/LCSD (BS/BSD) sets), its approval by the respective department manager, and by approval of the QA Department. Acceptable demonstration is added to the analyst’s training file.

12.4.9 Another “Demonstration of Capability Authorization/Certification Statement” must also be completed.

12.5 Control Limits (Procedure/Method Acceptance Criteria)

12.5.1 Once control limits have been established (in-house or by method), they are verified, reviewed, and updated if necessary on an annual basis unless the method or regulatory authority requires more frequent updating. Control limits are established per method (as opposed to per instrument) regardless of the number of instruments utilized.

12.5.2 More information concerning Control Limits can be found in Section 24.6 of the QA Manual.

12.5.3 Internal Quality Control Procedures. As part of the quality assurance program, the laboratory shall adhere to all stated QA/QC requirements in the method used. Any deviations from the method shall be documented. Deviations that result in nonconforming work shall be evaluated. The following QC checks will be performed per batch of samples:

12.5.4 Accuracy and bias. Accuracy studies are performed to determine how close a measurement comes to an actual or a theoretical value. Accuracy can be expressed as percent recovery and evaluated by analysis of laboratory control samples (LCS). Bias is a systematic error manifested as a consistent positive or negative deviation from the true value. The bias can be found in the original validated method by NIOSH.

12.5.5 Precision. Precision is evaluated by the reproducibility of analyses and it is commonly expressed as a relative percent difference. It can be evaluated by the analysis of laboratory control sample and laboratory control sample duplicate (LCS/LCSD).

12.5.6 Blank sampling media and analytical reagents will be analyzed with each batch of samples. At least one field blank should be used for each day of field sampling, shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the tube.

12.5.7 Reporting Field Blanks. The final report shall state the measured quantitative result of the field blanks submitted to the laboratory. Also, the laboratory should disclose whether or not the sample results have been corrected for contamination based on the field blank or other analytical blank.

12.5.8 Reporting levels are determined for the initial desorption/validation study. The reporting level for each analyte can be found in Attachment 1. If results for the LCS/LCSD pair

are not within the appropriate specifications, then the problem must be resolved. If references are prepared, the resulting amount found for the reference should be compared to the target for the respective spikes, just to make sure there are no significant differences or problems.

12.6 Measurement Uncertainty

12.6.1 Uncertainty is “a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurement” (as defined by the International Vocabulary of Basic and General Terms in Metrology, ISO Geneva, 1993, ISBN 92-67-10175-1). The minimum uncertainty associated with results generated by the laboratory can be determined by using the Laboratory Control Sample (LCS) accuracy range for a given analyte. The LCS limits are used to assess the performance of the measurement system since they take into consideration all of the laboratory variables associated with a given test over time (except for variability associated with the sampling and the variability due to matrix effects). The percent recovery of the LCS is compared either to the method-required LCS accuracy limits or to the statistical, historical, in-house LCS accuracy limits.

12.6.2 To calculate the uncertainty for the specific result reported, multiply the result by the decimal of the lower end of the LCS range percent value for the lower end of the uncertainty range, and multiply the result by the decimal of the upper end of the LCS range percent value for the upper end of the uncertainty range. These calculated values represent a 99%-certain range for the reported result. As an example, suppose that the result reported is 1.0 mg/l, and the LCS percent recovery range is 50 to 150%. The uncertainty range would be 0.5 to 1.5 mg/l, which could also be written as 1.0 ± 0.5 mg/L.

12.6.3 Refer to the Quality Assurance Manual for further discussion of uncertainty.

13.0 Pollution Control

13.1 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 Section 13 – Waste Management and Pollution Prevention of the Corporate Environmental Health and Safety Manual (CW-E-M-001) or the current Waste Management SOP.

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

14.2.1 Autosampler vial waste (Open Top Metal Drum): The used vials will be collected and stored in labeled containers located in the fume hood cabinets. When the containers are full, they will be transported in the same container to the storage area. The vials will then be safely and gently transferred to the drum, via a funnel to minimize fumes during removal of the drum lid, ensuring no vial breakage.

14.2.2 Mixed solvent waste (Closed Top Metal Drum): Solvent waste is stored in appropriately labeled hazardous waste containers in satellite storage areas throughout the lab, and should be emptied as often as possible. The waste should be transferred to the storage area in these exact same containers. The snorkel valve on the fume hood exhaust tubing should be turned 90 degrees clockwise to direct flow to the snorkel. The drum openings should then be opened with a wrench. The carboy placed over one opening and the snorkel placed over the other opening. The valve for the carboy should then be opened thereby transferring the contents of the carboy into the waste drum.

14.2.3 Contaminated solid material utilized for sample preparation (i.e. glass ASE vials, transfer pipettes, plastic materials, sodium sulfate). If the solid material is estimated to contain <5% of the original material, they can be disposed of in the trash, unless they exhibit RCRA characteristics such as ignitability, reactivity, corrosivity or toxicity.

14.2.4 Expired primary and working standards:

- I. Low concentration (<1000PPM): Dispose of in the solvent waste stream.
 - a. If the standard is prepared in water, dispose in the acidic waste stream.
- II. High concentration: (>1000 PPM) Lab pack.

14.3 Any waste, which does not fit into any of the waste streams or cannot be disposed of in any of the other drums, should be brought directly to the department and/or waste manager's attention.

15.0 References / Cross-References

15.1 NIOSH Method 5506, Issue 3, dated 15 January 1998.

15.2 TestAmerica Laboratories, Inc.

- Environmental Health and Safety Manual, CW-E-M-001.

15.3 TestAmerica – Phoenix

- Quality Assurance Manual, PX-QAD-011.
- SOP PE-SFT-001 Sample Disposal and Waste Management.
- SOP PE-QAD-008 Personnel Certification and Training.
- SOP PE-QAD-013 Reagent and Standard Preparation, Control, and Documentation.
- PX-QAD-007 Training Documentation Form.
- PX-QAD-069 Group Training Documentation Form.

15.4 AIHA Policies for Laboratory Quality Assurance Programs, September 13, 2011.

16.0 **Method Modifications:**

Item	Method	Modification
1	NIOSH 5506	Supelcosil LC-PAH column, 15 cm x 4.6 mm, 5 µm (PN# 58318) or equivalent. Phenomenex SecurityGuard cartridge system (PN# KJO-4282) or equivalent and Guard Column, C18 (ODS, Octadecyl) 4mm LX 3.0 mm ID (PN# AJO-4287) or equivalent. (Use of updated columns is not considered a modification to the method per AIHA.)

17.0 **Attachments**

Attachment 1: Analyte Reporting Levels and Sampling Rates
Attachment 2: Analyte Concentrations In Highest Working Standard
Attachment 3: Analyte Detectors
Attachment 4: Analytical Data Review Checklist

18.0 **Revision History**

Revision 0, dated April 3, 2008

- Integration of TestAmerica and STL operations.

Revision 1, dated May 19, 2010

- Conversion to the TestAmerica Laboratories, Inc. SOP template.

Revision 2, dated May 25, 2012

- Biannual SOP Review.
- Section 5 – added safety information regarding the use of an HPLC.
- Section 7 – added reference to SOP PE-QAD-013 in section 7.6.
- Section 14 Waste Management – updated to current information.
- Section 15 References/Cross References – updated.

Attachment 1: Analyte Reporting Levels and Sampling Rates

Chemical Name	OSHA PEL TWA STEL	NIOSH REL TWA STEL	ACGIH TLV TWA STEL	Sampling Rates (L/min)	Air Volume (L)	Reporting Level (µg/sample)
Naphthalene	50 mg/m ³ No STEL	50 mg/m ³ 75 mg/m ³	52 mg/m ³ 79 mg/m ³	2	200 - 1000	1
Acenaphthylene	N/A	N/A	N/A	2	200 - 1000	2.5
Acenaphthene	N/A	N/A	N/A	2	200 - 1000	2
Fluorene	N/A	N/A	N/A	2	200 - 1000	0.5
Phenanthrene	0.2 mg/m ³	N/A	N/A	2	200 - 1000	0.25
Anthracene	0.2 mg/m ³	N/A	N/A	2	200 - 1000	0.25
Fluoranthene	N/A	N/A	N/A	2	200 - 1000	0.5
Pyrene	0.2 mg/m ³	N/A	N/A	2	200 - 1000	0.25
Benzo(a)anthracene	N/A	N/A	N/A	2	200 - 1000	0.25
Chrysene	0.2 mg/m ³	N/A	N/A	2	200 - 1000	0.25
Benzo(b)fluoranthene	N/A	N/A	N/A	2	200 - 1000	0.5
Benzo(k)fluoranthene	N/A	N/A	N/A	2	200 - 1000	0.25
Benzo(a)pyrene	0.2 mg/m ³	N/A	N/A	2	200 - 1000	0.25
Dibenzo(a,h)anthracene	N/A	N/A	N/A	2	200 - 1000	0.5
Benzo(g,h,i)perylene	N/A	N/A	N/A	2	200 - 1000	0.5
Indeno(1,2,3)pyrene	N/A	N/A	N/A	2	200 - 1000	0.25

NIOSH 5506 is the method reference. Sample stability was not determined by NIOSH.

Definitions of acronyms and abbreviations in Attachment 1:

PEL = Permissible Exposure Limit

REL = Recommended Exposure Limit

STEL = Short Term Exposure Limit (usually based on 15-minute sampling period)

TLV = Threshold Limit Value

TWA = Time-Weighted Average (usually based on 8-hour workday)

OSHA = Occupational Safety and Health Administration

ACGIH = American Conference of Governmental Industrial Hygienists

L/min = Liters per Minute

mg/m³ = milligrams per cubic meter (air concentration)

Attachment 2

ANALYTE CONCENTRATIONS IN HIGHEST WORKING STANDARD

Analyte	Concentration (µg/mL)
Naphthalene	20
Acenaphthylene	40
Acenaphthene	20
Fluorene	4.0
Phenanthrene	2.0
Anthracene	2.0
Fluoranthene	4.0
Pyrene	2.0
Benzo(a)anthracene	2.0
Chrysene	2.0
Benzo(b)fluoranthene	4.0
Benzo(k)fluoranthene	2.0
Benzo(a)pyrene	2.0
Dibenzo(a,h)anthracene	4.0
Benzo(g,h,i)perylene	4.0
Indeno(1,2,3)pyrene	2.0

Attachment 3

Chemical Name	<i>Detector</i>
Naphthalene	UV
Acenaphthylene	UV
Acenaphthene	UV
Fluorene	UV
Phenanthrene	UV
Anthracene	UV
Fluoranthene	FL
Pyrene	FL
Benzo(a)anthracene	FL
Chrysene	UV
Benzo(b)fluoranthene	FL
Benzo(k)fluoranthene	FL
Benzo(a)pyrene	FL
Dibenzo(a,h)anthracene	FL
Benzo(g,h,i)perylene	FL
Indeno(1,2,3)pyrene	FL

Attachment 3

ANALYTICAL DATA REVIEW CHECKLIST

**SOP PE-IHD-008 R.2
Modified NIOSH 5506**


Analysis Date:		Batch #:		Analyst:		
Description				Yes	No	NA ¹
1. Calibration Curve (7 levels are typical, 3 levels minimum)						
- All target compounds ($r > 0.995$)						
- Date of Initial Calibration:						
2. Opening ICV (Second Source Standard)						
- Reporting Level ICV ($\pm 40\%$ of target)						
3. Continuing Calibration Verification (CCV) (Primary Standard)						
- CCV near highest standard concentration ($\pm 20\%$ of target)						
- Every 10 samples and at end of analysis						
4. Method Blank						
- Analyze one FILTER Blank per batch						
- Analyze one TUBE Blank per batch						
5. LCS/LCSD prepared and analyzed with each batch (independently prepared or second source standard)						
- One pair per batch						
- All recoveries are 50 – 150% and $\leq 50\%$ RPD or historical						
6. Calibration Blank/Continuing Calibration Blank (CB/CCB)						
- $< RL$						
- Every 10 Samples, one before/following opening CCV and at end of analysis						
Comments:						
CAR #						
Review Signatures:	Analyst:		Date:			
	Reviewer:		Date:			


¹⁾ NA: Not Applicable

SULFIDE: TITRIMETRIC PREPARATION AND ANALYSIS
(Total and Acid Soluble)

(Methods: EPA 376.1, EPA 9030B, and EPA 9034 and SM4500-S²⁻ F)

Approvals (Signature/Date):

 May 5, 2011
Date
Andrea Teal
Quality Assurance Manager

 January 20, 2011
Date
Benjamin Gulizia
Laboratory Director/Lead Technical Director

 February 25, 2011
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-S²⁻ F. Note: Based on the 2007 Method Update Rule, EPA Method 376.1 is not approved for NPDES work. Standard Methods 4500-S²⁻ F is the approved NPDES method.

3.0 Definitions

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.

- 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 (H₂S) 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.

¹Exposure limit refers to the OSHA regulatory exposure limit.

Note: Always add acid to water to prevent violent reactions.

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

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.

- 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 [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] – 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,

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 H_2SO_4 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

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 $180^\circ C$ 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:

$$N(KIO_3) = \frac{A}{35.67g/eq \otimes 0.25L}$$

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.

7.2.19.1 Rinse a 10mL burette with the Sodium Thiosulfate Solution ($\text{Na}_2\text{S}_2\text{O}_3$). Fill the burette with the $\text{Na}_2\text{S}_2\text{O}_3$.

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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ as follows:

$$N = \frac{A \otimes B}{V}$$

Where:

A = mL of KIO_3 titrated

B = N of KIO_3

V = mL $\text{Na}_2\text{S}_2\text{O}_3$ 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 ($\text{Na}_2\text{S}_2\text{O}_3$) 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.

- 7.2.21.1 Rinse the 10mL burette with the standardized $\text{Na}_2\text{S}_2\text{O}_3$. Fill the burette with the standard $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ required for each standardization in the Standardization Log.

- 7.2.21.5 Calculate the normality (N) of the I_2 solution as follows:

$$N(\text{I}_2) = \frac{A \otimes B}{V}$$

Where:

A = mL of standard $\text{Na}_2\text{S}_2\text{O}_3$

B = normality of standard $\text{Na}_2\text{S}_2\text{O}_3$

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 Standards

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 ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) – reagent grade. This solid must be stored in a dessicator at all times.

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 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ 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-prepare 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-S²⁻ 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

- 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 $\text{Na}_2\text{S}_2\text{O}_3$. Fill the burette with the $\text{Na}_2\text{S}_2\text{O}_3$ to prepare for titration. Note: 0.025N standardized $\text{Na}_2\text{S}_2\text{O}_3$ is used for EPA 376.1 and SM4500-S²-F. The 0.00625N titrant is used for EPA 9030/9034 micro-distilled samples.

10.3.3 For EPA 376.1 and SM4500-S²-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-S²-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

than 2. If the pH is less than 2 and the solution has turned colorless, add 0.10N I₂ 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 Na₂S₂O₃ 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:

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

$$\frac{mg\ S}{kg}, dw = \frac{(A \otimes B) - (C \otimes D)}{\frac{W \otimes solids}{FV} \otimes V_t} \otimes \frac{32.06\ mg\ S}{2\ meq\ I_2} \otimes \frac{1000\ g}{1\ kg}$$

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)

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

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

- *Standard Methods for the Examination of Water and Wastewater*; Online Edition; American Public Health Association: Washington, DC
 - SM4020: *Quality Assurance/Quality Control*
 - SM4500-S²⁻ 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., LCS 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-S²⁻ 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.

**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

¹Unless noted, holding time is from collection to analysis

²From collection to distillation

³From distillation to analysis

**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

QC Item	Frequency	Criteria	Corrective Action
Verification (RLV)	analyte/method/matrix combination. Then quarterly thereafter (for DOD ELAP) or annually thereafter (for NELAC)		

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.

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 clear determination. Section 10.3.14

Title: CYANIDE PREPARATION METHOD

[Method: EPA Methods 335.1, 335.2, 335.2(CLP-M), 335.4, Standard Method 4500-CN-I, 4500-CN-E, 4500-CN-G, and SW846 Method 9012A]

This revision is not applicable for Ohio VAP projects

Approvals (Signature/Date):


Technology Specialist 04/05/12
Date


Health & Safety Coordinator 04/16/12
Date


Quality Assurance Manager 04/13/12
Date


Laboratory Director 03/27/12
Date

This SOP was previously identified as SOP No. NC-WC-032, Rev 8.7, dated 06/06/10

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Total, Amenable, and Weak Acid Dissociable in solids, liquids, and waters. It is based on SW 846 Method 9012A, EPA 335.1, 335.2, 335.2 (CLP-M) Ohio VAP only, 335.4, and Standard Methods 4500-CN-E, 4500-CN-G and 4500-CN-I. The working linear range is 0.005 - 0.2 mg/L for waters and 0.25 to 10 mg/kg for solids.
- 1.3. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary by the laboratory.

2. SUMMARY OF METHOD

- 2.1. The Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid and is trapped in a sodium hydroxide solution.

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

- 4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks (MBs) as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Interferences are eliminated or reduced by using the distillation procedure. Oxidizing agents, such as chlorine, will decompose most cyanides. Sulfide will distill over with the cyanide and could affect colorimetric, titrimetric, and electrode procedures. Refer to the preparation section on how to screen and treat samples appropriately. The possibility of interferences from nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation.
- 4.3. Aldehydes convert cyanide to cyanohydrin which could result in the loss of cyanide. If the presence of aldehydes are suspected, stabilize the sample with NaOH at the time of collection and add 2 mL 3.5% ethylenediamine solution per 100 mL of sample.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and

Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.

- 5.2. In the event the sample begins to react unexpectedly during distillation, remove entire apparatus from heat source, set aside, and allow to cool. **DO NOT ATTEMPT TO DISASSEMBLE GLASSWARE.** Doing so may result in a sudden release of pressure with spraying of the sample.
- 5.3. Latex, vinyl, nitrile, or similar gloves may be used.
- 5.4. Preparation of sodium hydroxide solutions produces considerable amounts of heat. Use plastic containers to mix this solution if possible. If glass containers are used, they must be free of any cracks or irregularities.
- 5.5. The acidification of samples prior to extraction/preparation can result in the release of a highly toxic gas, hydrogen cyanide.
- 5.6. If samples are identified with cyanide concentrations equal to or greater than 200 mg/L, immediately notify the Department Manager and personnel responsible for hazardous waste shipping. Those samples must be identified as extremely hazardous for other chemists and must receive special attention during disposal. **Potassium cyanide and sodium 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.**
- 5.7. Cyanide and cyanide salts are extremely toxic. Addition of acid can generate hydrogen cyanide gas, which can be extremely dangerous.
- 5.8. 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
Potassium Cyanide	Poison Corrosive	5 mg/m ³ 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.
Ascorbic Acid	Slight Health, Reactivity, Flammability, and Contact	No PEL Est	May cause mild irritation to the respiratory tract
Acetic Acid (1)	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.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Cadmium Carbonate	Probable carcinogen	0.01 mg/ m ³ as Cd	Ingestion causes increased salivation, choking, vomiting, stomach pains and diarrhea. Inhalation may cause respiratory irritation, nausea and dyspnea.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m ³ 2 mg/m ³ -Ceiling	This material will cause burns if comes into contact with the skin or eyes. 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.
Magnesium Chloride	Health	No PEL est.	Inhalation of dust may cause mild irritation to the mucous membranes.
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.

Sulfamic Acid	Corrosive Poison	No PEL est.	Symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea and vomiting. Can be fatal if ingested.
Sodium Cyanide	Poison Corrosive	5 mg/m ³ TWA as CN (skin)	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 heartbeat, 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.
Zinc Acetate	Irritant	None Listed	Symptoms of skin or eye contact include redness, itching and pain.
Silver Nitrate	Corrosive Poison Oxidizer	0.01 mg/m ³ (TWA) for silver metal dust and fume as 0.02 Ag	This is a corrosive, poisonous material. It will cause burns to any area of contact and is harmful if inhaled. Ingestion may cause death. Contact with other material may cause fire. Inhalation symptoms may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea, and vomiting. May be absorbed into the body following inhalation. Swallowing can cause severe burns of the mouth, throat and stomach. Can cause sore throat, vomiting, and diarrhea. Poison. Symptoms include pain and burning in the mouth, blackening of the skin and mucous membranes, throat, and abdomen, salivation, vomiting of black material, diarrhea, collapse, shock, coma and death. Skin contact can cause redness, pain and severe burns. Eye contact can cause blurred vision, redness, pain, severe tissue burns and eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

- 5.9 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded; other gloves must be cleaned immediately.
- 5.10 Exposure to chemicals must be maintained **as low as reasonably achievable**. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.
- 5.11 The preparation of standards and reagents must be conducted in a fume hood with the sash closed as far as the operation will permit.

- 5.12 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and Laboratory Supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. Cyanide Distillation Apparatus
- 6.2. Analytical balance, capable of accurately weighing ± 0.0001 g
- 6.3. Vacuum source
- 6.4. Graduated cylinders: 50 mL
- 6.5. Volumetric flasks: 100 mL, 200 mL, 500 mL, 1 L
- 6.6. Volumetric pipettes: range from 0.01 to 20 mL
- 6.7. Balance: Top loading, capable of accurately weighing ± 0.01 g
- 6.8. Lead Acetate Indicator Paper
- 6.9. Potassium Iodide (KI) Indicator Paper
- 6.11. Buret: Class A 10 mL
- 6.12. pH strips
- 6.13. Snap seal containers: 120 mL
- 6.14. Plastic bottles with lids: 250mL or 500mL

7. REAGENTS AND STANDARDS

- 7.1. Reagents
 - 7.1.1. Sulfamic Acid: reagent grade
 - 7.1.2. Sulfamic Acid Solution: Add 100 g of sulfamic acid to 800 mL reagent water and dilute to 1 liter with reagent water
 - 7.1.3. Ascorbic Acid: reagent grade
 - 7.1.4. Sodium Hydroxide: (NaOH), high purity grade.

- 7.1.5. Sodium Hydroxide, 0.25 N: Add 10 g of NaOH to 900 mL reagent water and dilute to 1 liter with reagent water. Purchased reagent may also be used.
- 7.1.6. Sulfuric Acid: (H₂SO₄), concentrated
- 7.1.7. Acetic Acid Solution: Add 200 mL of reagent water to a 1.0 L volumetric flask. Carefully add 750 mL of glacial acetic acid, and bring to volume with reagent water. Transfer to a 1.0 L amber bottle and cap.
- 7.1.8. Magnesium Chloride: (MgCl₂•6H₂O), reagent grade.
- 7.1.9. Magnesium Chloride Solution: Add 510 g MgCl₂•6H₂O to 500 mL reagent water and dilute to 1 liter with reagent water. Purchased reagent may also be used.
- 7.1.10. Calcium Hypochlorite: [Ca (OCl)₂], reagent grade
- 7.1.11. Calcium Hypochlorite Solution: Add 5 g of Ca(OCl)₂ to 100 mL of reagent water. Store in an amber glass bottle in the dark. Prepare monthly.
- 7.1.12. Methyl Red Indicator: Add 0.25 g of methyl red to 250 mL of glacial acetic acid and dilute to 500 mL with reagent water.
- 7.1.13. Methyl red reagent grade glacial
- 7.1.14. Acetic Acid: (CH₃COOH), glacial reagent grade
- 7.1.15. Zinc Acetate: [Zn(C₂H₃O₂)], reagent grade
- 7.1.16. Zinc Acetate Solution: Add 100 g zinc acetate to 800 mL reagent water and dilute to 1 liter with reagent water.
- 7.1.17. Sodium Acetate: [NaC₂H₃O₂•3H₂O] reagent grade
- 7.1.18. Sodium Acetate Buffer: Add 410 g of sodium acetate to 500 mL of reagent water. Adjust the pH to 4.5 using glacial acetic acid and dilute to 1 liter with reagent water.
- 7.1.19. Rhodanine: reagent grade
- 7.1.20. 0.0192 N Silver Nitrate: reagent grade
- 7.1.21. Cadmium carbonate [CdCO₃]: reagent grade
- 7.2. Standards

- 7.2.1. Primary Source Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well and store in glass amber container. Stable for 1-3 months. Additional information can be found in SOP NC-QA-017.

Note: This stock standard may also be purchased.

Note: Prepared stock standard must be standardized prior to use. See Appendix I

- 7.2.2. Secondary Source Cyanide Standard, 1000 mg/L: Follow Section 7.2.1 using an alternate source of Potassium Cyanide (KCN).

Note: This stock standard may also be purchased.

Note: Prepared stock standard must be standardized prior to use. See Appendix I.

- 7.2.3. Calibration Standards (Water and Solid Matrices)

7.2.3.1 If using the purchased 0.25N NaOH: Pipette the appropriate amount of cyanide standard into 100 mL volumetric, and bring to volume with 0.25N NaOH. Prepare weekly.

Concentration CN-	ML CN-	Final Volume
10 mg/L	10 mL of 100 mg/L	100 mL
1.0 mg/L	20 mL of 10 mg/L	200 mL

8. SAMPLE PRESERVATION AND STORAGE

- 8.1. Solid and liquid samples are not chemically preserved. Water samples are preserved with NaOH to a pH>12. All samples are stored at 4° C ± 2°C in plastic or glass containers.
- 8.2. The holding time for samples is 14 days from sampling to analysis.

9. QUALITY CONTROL

- 9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples excluding QC samples (Laboratory Control Sample (LCS), Method Blank(MB), Matrix Spike (MS), Matrix Spike Duplicate (MSD)) which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the

same lots of reagents and the same process.

9.2. Method Blank (MB)

9.2.1. One method blank (MB) must be processed with each preparation batch. The method blank (MB) must contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank (MB) is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank (MB) must not contain any analyte of interest at or above the reporting limit.

9.2.1.1. A method blank (MB) consists of 50 mL 0.25N NaOH for Total Cyanide analysis or 50 mL reagent water for Weak Acid Dissociable and Amenable Cyanide analysis. The method blank (MB) for solids consists of 50 mL 0.25N NaOH or reagent H₂O and 1.0g Ottawa sand. The method blank (MB) must be distilled per Section 11.4.3 and analyzed with each analytical batch of samples.

9.2.2. Corrective Action for Method Blanks (MBs)

9.2.2.1. If the analyte level in the method blank (MB) exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative**.

9.2.2.2. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank (MB), the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One Laboratory Control Sample (LCS) must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure. The laboratory control sample (LCS) is used to monitor the accuracy of the analytical process. Ongoing monitoring of the laboratory control sample (LCS) results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. For Method 335.1, laboratory control sample (LCS) recoveries must be within 90% to 110%, or corrective action is required.

9.3.2. A mid-range laboratory control sample (LCS) consisting of a 0.04 mg/L (2.0 mL of 1.0 mg/L secondary source to 50 mL) must be distilled per Section 11.4.3 and analyzed with each analytical batch of samples for Total, Non-Amenable, and Weak Acid Dissociable Cyanide analysis.

Note: A purchased complex cyanide solution may be used instead as the midrange laboratory control sample (LCS) for **Total Cyanide** analysis only.

9.3.3. Corrective Action for Laboratory Control Samples (LCS)

9.3.3.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.

9.3.3.2. Corrective action must be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable. For Ohio VAP samples, the laboratory control sample (LCS) must be redistilled, unless the laboratory control sample (LCS) is biased high and the samples are non-detect.

9.3.3.2 The only exception is that if the laboratory control sample (LCS) recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

9.4 Additional information on QC samples can be found in QA Policy QA-003.

9.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.5.1 One matrix spike/matrix spike duplicate (MS/MSD) pair must be processed for each batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to matrix spike/matrix spike duplicates (MS/MSDs). The matrix spike duplicate (MS/MSD) results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for matrix spike/matrix spike duplicate (MS/MSD) analysis.

9.5.1.1 A matrix spike/matrix spike duplicate (MS/MSD) consisting of 50 mL or 1.0g of sample brought up to 50 mL with reagent water and 2.0 mL of the 1.0 mg/L of secondary standard must be distilled with each analytical batch of samples. For samples requiring Amenable analysis, a matrix spike/matrix spike duplicate (MS/MSD) consisting of 50 mL or 1 g of sample brought up to 50 mL with reagent water must be prepared and carried through all steps of the Amenable process. After distillation, the distillate is spiked with 2 mL of the 1ppm standard. The same sample must have a total cyanide matrix spike/matrix spike duplicate (MS/MSD) performed. The difference is calculated and reported.

9.5.2 Corrective action for Matrix Spike/Matrix Spike Duplicates (MS/MSDs)

9.5.2.1 If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the laboratory control sample (LCS). If the laboratory control sample (LCS) recovery is within control limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the laboratory control sample (LCS) is outside control limits, corrective action must be taken. Corrective action must include re-preparation and re-analysis of the batch.

9.5.2.2 If the native analyte concentration in the matrix spike/matrix spike duplicate (MS/MSD) exceeds four times the spike level for that analyte, the recovery data is flagged with a "4" in LIMS.

9.5.2.3

9.6 Control Limits

9.6.1 Control limits are established by the laboratory as described in SOP NC-QA-018, with the exception of Method 335.1 which has stated control limits for the laboratory control sample (LCS), matrix spike (MS), and matrix spike duplicate (MSD) of 90% to 110%.

9.6.2 Laboratory control limits are internally generated and updated periodically unless method specified. Control limits are easily accessible via LIMS

9.7 Method Detection Limits (MDLs) and MDL Checks

9.7.1 MDLs and MDL Checks are established by the laboratory as described in SOPs NC-QA-021 and CA-Q-S-006.

9.7.2 MDLs are easily accessible via LIMS .

9.8 Nonconformance and Corrective Action

9.8.1 Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1 A low and high standard are distilled from the same source as the calibration curve each day. Prepare the low standard (0.025 mg/L) by diluting 0.125 mL of 10 ppm standard with 0.25N NaOH to a final volume of 50 mL. Prepare the high standard (0.1 mg/L) by diluting 0.5 mL of 10 ppm standard with 0.25N NaOH to a final volume of 50 mL. If distilled standards do not agree within 10% of the undistilled standards, the analyst must find the cause of the apparent error before proceeding. The instrument is calibrated daily using the 0.2 ppm standard (see SOP NC-WC-031), which is diluted by the instrument into the following concentrations: 0.005, 0.010, 0.025, 0.050, 0.100, 0.200.

11. PROCEDURE

11.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo. The Nonconformance Memo must be filed in the project file. This is not applicable for Ohio EPA/VAP.

11.4. Sample Preparation Procedure applicable for use with the Midi distillation unit.

11.4.1 For DoD work, refer to SOP NC-QA-016 for specific details.

11.4.2 Checking for Interferences

11.4.2.1. Using pH paper strips, check the pH of the sample and document in the LIMS worksheet if the pH is <12. If pH is <12, the deviation **must be addressed in the project narrative.**

11.4.2.2. Test each sample for the presence of sulfides using lead acetate paper. If sulfides are present, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution. Avoid a large excess of cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material. **If any sample in a batch is treated, the Method Blank (MB) and Laboratory Control Sample (LCS) for the batch must undergo the same treatment.** Document this in LIMS

NOTE: If Sulfide is present, and more than 48 hours have elapsed since sampling, the analyst must create an NCM notifying the client of the presence of Sulfide.

11.4.2.3 Test each sample for the presence of chlorine using potassium iodide test strips. If chlorine is present, add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. **If any sample in a batch is treated, the Method Blank (MB) and Laboratory Control Sample for the batch must undergo the same treatment.** Document this in LIMS

11.4.3 Amenable Cyanide (Chlorinated Aliquot)

11.4.3.1. Place 50 mL (waters) or 1.0 g (solids/liquids) into a snap cap container. Add 50 mL of reagent water to non-waters. Place the snap cap container on a stir plate and begin mixing. Test the pH of the solution. If less than 12, add 1.25 N NaOH, drop by drop until pH \geq 12. Drop by drop, add calcium hypochlorite until an excess of chlorine is reached. Test for chlorine excess using KI paper. Allow the sample to chlorinate for one hour maintaining

excess chlorine and pH between 11 and 12. If necessary, add more $\text{Ca}(\text{OCl})_2$ and/or NaOH. Either cover snap cap containers with aluminum foil, or place box over snap cap containers to keep them in the dark during the chlorination process. At the end of the chlorination period, add about 0.1 to 0.5 g of ascorbic acid to destroy excess chlorine. Test using KI paper. Keep the addition of ascorbic acid to a minimum. Pour the sample into a distillation flask and follow the total cyanide preparation method (Section 11.4.3). Also set up an unchlorinated aliquot of sample (50 mL or 1.0 g) following the total cyanide method.

Reminder: Do not use the purchased complex cyanide standard for the Amenable Laboratory Control Sample (LCS).

11.4.4 Total Cyanide

- 11.4.4.1 Add 50 mL or 1.0 g of the sample to the distillation tube. Bring the final volume to 50 mL with reagent water. Add 25 mL of 0.25 N NaOH solution to the collection trap. Assemble the cyanide distillation apparatus.
- 11.4.4.2 Waste Procedure - Sometimes waste samples will stick to the weigh pan making it difficult to rinse all of the sample into the distillation tube, causing a biased low result. In this case, aliquot the sample onto a Whatman 47mm filter instead of a weigh pan. If the sample is bleeding through the filter, use extra filters to prevent sample loss due to over-saturation of the filter. It may be helpful to form the filter into a bowl shape before aliquoting to keep the it from running off the filter. Once the sample is weighed, the filter can be wrapped around the sample and dropped into the distillation tube. When preparing waste samples in this way, an extra blank must be distilled with a filter added to the distillation tube. This blank must be analyzed and shown to be free of cyanide to prove the filters do not contain cyanide. Proceed with the rest of the distillation as usual.
- 11.4.4.2 Turn on the vacuum source and adjust the flow such that the bubbles in the collection trap are steady (~10bubbles/second) but not bubbling so fast that the NaOH is splashing in the collection trap. At this time, add any spiking solutions to the laboratory control sample (LCS) or matrix spike/matrix spike duplicates (MS/MSDs)samples directly into the inlet tube.
- 11.4.4.3 In the order stated, add 2.0 mL sulfamic acid solution, 2.5 mL of concentrated sulfuric acid, and 2.0 mL of magnesium chloride solution to the distillation tube. Be sure to rinse the inlet tube sparingly with reagent water between and after reagent additions.
- 11.4.4.4 Flip the heater switch to “on” to allow the apparatus to warm up. Be sure to adjust the air flow and water as necessary. Heat for one hour. Allow to cool for 15 minutes. Keep the vacuum on.

- 11.4.4.5 Disconnect the absorber. Pour solution into a 120 mL snap seal container or place the collection trap into designated Styrofoam holders. Check the pH of the solution to ensure it is >12 . **NOTE:** If the pH is not >12 , do NOT remove the sample from the hood. Contact the Technical Director, Operations Manager, or EH&S representative immediately for further instruction. Do not rinse the scrubber tube or dilute NaOH in the snap seal. Be sure to properly label the bottles "total" or "amenable" along with sample ID, position, and date.

11.4.5 Weak Acid Dissociable

- 11.4.5.1 Add 50 mL or 1.0 g of sample to the distillation tube. Bring all volumes up to 50 mL with reagent water. Add 25ml 0.25N NaOH solution to the collection trap and assemble.

- 11.4.5.2 Turn on the vacuum source. Add any spiking standards to the appropriate laboratory control sample (LCS) or matrix spike/matrix spike duplicates (MS/MSDs) at this time. Through the inlet tube, add 1.0 mL of sodium acetate buffer, 1.0 mL of zinc acetate, and 0.25 mL of methyl red indicator. Rinse the inlet tube sparingly with reagent water between and after reagent additions. If the sample is not red, carefully add 75% acetic acid drop-wise until the sample does turn red. Check the sample color periodically throughout the distillation hour to ensure the sample stays red.

Reminder: Do not use the complex purchased cyanide solution standard as the laboratory control sample (LCS) for Weak Acid Dissociable cyanide analysis.

- 11.4.5.3 Flip on the heater switch (this allows the apparatus to warm up). Adjust the air flow and water as needed. Heat for one hour. Allow the sample to cool for 15 minutes with the air and water on.
- 11.4.5.4 Pour the scrubber contents into a 120 mL snap seal bottle or place collection traps in designated Styrofoam holders. Do not rinse the scrubber. Label the bottle well, and be sure to denote it is a Weak Acid Dissociable sample distillate.

11.4.6 Cyanide Unit Cleanup

- 11.4.6.1 Cyanide distillation unit glassware is very fragile and expensive. It must be handled with care at all times.
- 11.4.6.2 Disassemble each setup. Be sure to collect the solids in a screen and dispose of properly.
- 11.4.6.3 Wash each setup with hot water. Rinse several times with reagent water.

Note: After preparing samples found to be extremely high in cyanide, distill 0.25 N NaOH through the system.

11.4.6.4 Re-assemble the setup.

11.4.6.5 Be sure to wash each setup as a separate unit, and replace in the same position. Wait for cyanide results before cleaning the glassware.

11.4.6.6 If a sample of known high cyanide concentration was distilled in a certain position, be sure to change the appropriate tubing on that position. Dispose plastic inlet tubes on any sample that was a hit for cyanide and on all weak acid dissociable samples. Some samples may be non-detect for weak acid, but have a high concentration of complex cyanide that is not released unless total reagents are used.

11.5 Analytical Documentation

11.5.1 Record all analytical information appropriately in LIMS, including the analytical data from standards, blanks, laboratory control sample (LCSs), matrix spike/matrix spike duplicates (MS/MSDs), and any corrective actions or modifications to the method.

11.5.2 All standards are logged into the LIMS reagent module. All standards are assigned a unique number for identification.

11.5.3 Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4 Sample results and associated QC are transferred directly into LIMS from the instrument. Level I and Level II review is done in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Not applicable

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations

of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

- 14.1. 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".

15. WASTE MANAGEMENT

- 15.1 All waste must be disposed of in accordance with Federal, State and Local laws and regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees must abide by this method and the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2 Waste Streams Produced by the Method

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

15.2.1.1 Total cyanide waste is disposed of in the designated container labeled "Acid Waste". Weak Acid dissociable waste is disposed of in a designated container labeled "Weak Acid Dissociable Waste".

15.2.1.2 Standard Waste and High Concentration Samples: This waste is disposed of in the designated container labeled "High Cyanide/Basic Waste." NO ACID is added to this container.

- 15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by an annual refresher training.

16. REFERENCES

16. References.

16.1.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Total and Amenable Cyanide, Automated UV; Method 9012A

16.1.2. EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Methods 335.1, 335.4, 335.2, and 335.2(CLP-M)

- 16.1.3. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition; Weak Acid Dissociable Cyanide; Method 4500-CN-I
- 16.1.4. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition; Complex Cyanide; Method 4500-CN-E, 4500 CN-G
- 16.1.5. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition; Colorimetric Method; Method 4500-CN-E, 4500 CN-E
- 16.1.6. [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version
- 16.1.7. TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version
- 16.1.8. [Corporate Quality Management Plan \(CQMP\)](#), current version
- 16.1.9. Revision History

Historical File:		Revision 7.0: 03/19/98		Revision 8.4: 12/08/04
		Revision 8.0: 02/04/99		Revision 8.5: 05/30/08
		Revision 8.1: 03/20/00		Revision 8.6: 12/30/08
		Revision 8.2: 05/31/01		Revision 8.7: 06/16/10
		Revision 8.3: 06/17/03		

- 16.2. Associated SOPs and Policies, current version

- 16.2.1. QA Policy, [QA-003](#)
- 16.2.2. Glassware Washing, [NC-QA-014](#)
- 16.2.3. Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)
- 16.2.4. Method Detection Limits and Instrument Detection Limits, [NC-QA-021](#) and [CA-Q-S-006](#)
- 16.2.5. Supplemental Practices for DoD Projects, [NC-QA-016](#)
- 16.2.6. Standards and Reagents, [NC-QA-017](#)
- 16.2.7. Cyanide, Automated Method, [NC-WC-031](#)

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

- 17.1. Method Deviation [9012A, 335.1, 335.2, 335.2(CLP-M) Ohio VAP only]
- 17.1.1. The reflux distillation apparatus used is the midi distillation.
- 17.1.2. The volume of sample used is reduced to 50 mL vs. 500 mL using the midi-distillation apparatus.
- 17.1.3. Method of Standard Addition is not performed for samples with matrix interference (sulfides).
- 17.1.4. Solid and waste samples are analyzed according to 335.2(CLP-M).
- 17.1.5. According to Method 335.2 (CLP-M) section 7.2.2.1 a mid-range standard must be distilled and compared to the curve for each SDG [batch] with a recovery of $\pm 15\%$. The laboratory distills a high and low standard daily with a recovery requirement of $\pm 10\%$.

Appendix I

CYANIDE STANDARDIZATION

1. Pipette 10.0 mL of the 1000 ppm stock cyanide standard into a 250 mL Erlenmeyer flask and add 90 mL of reagent water.
2. Add 0.5 mL (10 drops) of Rhodanine indicator.
3. Titrate with 0.0192 N silver nitrate (using a micro burette) until the color changes from yellow to pink/orange.
4. Titrate a blank (100 mL reagent water) following Steps 2 and 3.
5. Calculation

$$\text{Cyanide, mg / L} = \frac{(\text{A} - \text{B}) (1000)}{\text{mL Cyanide Solution (10)}}$$

Where:

A = mL titrant for standard

B = mL titrant for blank

6. If the cyanide concentration is not 1000 ppm, adjust concentration accordingly.

Title: CYANIDE AUTOMATED, PYRIDINE-BARBITURIC ACID METHOD

This revision is not applicable for Ohio VAP projects

[Method: SW846 Method 9012A, EPA Methods 335.2, 335.2 (CLP-M), 335.4, and Standard Methods 4500-CN-E, 4500-CN-I, and 4500-CN-G]

Approvals (Signature/Date):

 Technology Specialist	<u>04/05/12</u> Date	 Health & Safety Coordinator	<u>04/26/12</u> Date
 Quality Assurance Manager	<u>04/13/12</u> Date	 Laboratory Director	<u>03/27/12</u> Date

This SOP was previously identified as SOP No. NC-WC-031, Rev 8.3, dated 06/15/10

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1. SCOPE AND APPLICATION

- 1.1. This method is applicable to the determination of Total, Amenable, and Weak Acid Dissociable Inorganic Cyanide in solids, liquids, and waters. It is based on SW846 Method 9012A, 335.2, 335.2(CLP-M), 335.4 and Standard Methods 4500-CN-E, 4500-CN-I, and 4500-CN-G. The working linear range is 0.005 – 0.2 mg/L for waters and 0.25-10 mg/kg for solids. Reporting limits are listed in Section 17.
- 1.2. This document accurately reflects current laboratory Standard Operating Procedures (SOP) as of the date above. All facility SOPs are maintained and updated as necessary.
- 1.3.

2. SUMMARY OF METHOD

- 2.1. The Cyanide, as HCN, is released by distilling/refluxing the sample with strong acid and is trapped in a sodium hydroxide solution.
- 2.2. The sodium hydroxide solution is analyzed colorimetrically on an autoanalyzer using the pyridine-barbituric acid method.

3. DEFINITIONS

- 3.1. Refer to the glossary in the TestAmerica North Canton Quality Assurance Manual (QAM), current version.

4. INTERFERENCES

- 4.1. Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. All glassware is cleaned per SOP NC-QA-014. Specific selection of reagents may be required to avoid introduction of contaminants.
- 4.2. Sulfides interfere, but can be eliminated by treating the sample with cadmium carbonate prior to analysis.

5. SAFETY

- 5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, the Facility Addendum to the Corporate EH&S Manual, and this document.
- 5.2. 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
Potassium Cyanide	Poison Corrosive	5 mg/m ³ 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.
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.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m ³ 2 mg/m ³ - Ceiling	This material will cause burns if comes into contact with the skin or eyes. 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.
Potassium Phosphate	Flammable	None	Inhalation causes severe irritation to the respiratory tract. Causes severe irritation possibly burns, to the skin. Symptoms include redness and severe pain. .

Sodium Phosphate		None	Inhalation may cause respiratory tract irritation. Can produce delayed pulmonary edema. Causes mild skin and eye irritation. Ingestion may cause gastrointestinal irritation.
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.
Cadmium Carbonate	Probable carcinogen	0.01 mg/ m ³ as Cd	Ingestion causes increased salivation, choking, vomiting, stomach pains and diarrhea. Inhalation may cause respiratory irritation, nausea and dyspnea.
Barbituric Acid	Irritant	Not established	Limited information. Inhalation may irritate respiratory tract. Causes skin and eye irritation. Must be treated as potential health hazard; do not ingest.
Potassium Hydroxide	Poison Corrosive Reactive	2 mg/m ³ – Ceiling	Inhalation symptoms may include coughing, sneezing, damage to the nasal or respiratory tract. High concentrations can cause lung damage. Swallowing may cause severe burns of mouth, throat and stomach. Other symptoms may include vomiting, diarrhea. Severe scarring of tissue and death may result. Contact with skin can cause irritation or severe burns and scarring. Causes irritation of eyes with tearing, redness, swelling. Greater exposures cause severe burns with possible blindness.
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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3.

- 5.4. Preparation of sodium hydroxide solutions produces considerable amounts of heat. Use plastic containers to mix this solution, if possible. If glass containers are used, they must be free of any cracks or irregularities.

- 5.5. The acidification of samples prior to extraction/preparation can result in the release of a highly toxic gas--hydrogen cyanide.
- 5.6. If samples are identified with cyanide concentrations equal to or greater than 200 mg/L, immediately notify the Department Manager and personnel responsible for hazardous waste shipping. Those samples must be identified as extremely hazardous for other chemists and must receive special attention during disposal.
- 5.7. Potassium cyanide and sodium 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.
- 5.8. Cyanide and cyanide salts are extremely toxic. Addition of acid can generate hydrogen cyanide gas, which can be extremely dangerous.
- 5.9. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut-resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated must be removed and discarded. Other gloves must be cleaned.
- 5.10. Exposure to chemicals must be maintained **as low as reasonably achievable**. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers must be kept closed unless transfers are being made.
- 5.11. It is recommended that neat standards be purchased only as a last resort. The preparation of standards from neat materials and reagents must be conducted in a fume hood with the sash closed as far as the operations will permit.
- 5.12. Standards in solution may be diluted in the open laboratory when syringes and the like are utilized.
- 5.13. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1. 2 mL and 4mL Cuvettes
- 6.2. 100 mL, 250 mL, 1000 mL volumetric flasks

6.3 Volumetric pipettes: various, ranging from 0.01 mL to 20 mL

6.4 Top loading balance: capable of accurately weighing ± 0.01 g

6.5 Balance: Analytical, capable of accurately weighing 0.0001g

7. REAGENTS AND STANDARDS

7.1. Reagents

7.1.1. Cadmium carbonate: powder

7.1.2. Phosphate buffer: Add 136 g of potassium phosphate - monobasic (KH_2PO_4) and 2.8 g of sodium phosphate – dibasic anhydrous (Na_2HPO_4) to 800 mL of reagent water in a 1 liter volumetric flask. Mix, bring to volume with reagent water (may be purchased commercially.)

7.1.3. Chloramine-T reagent: Add 1.0 g of chloramine-T to a 250 mL volumetric flask and dilute to volume with reagent water. Prepare fresh daily. (May be purchased commercially.)

7.1.4. Pyridine reagent: Add 15.0 g of barbituric acid to a 1 liter volumetric flask. Add 75 mL of pyridine and 15 mL of concentrated hydrochloric acid (HCl) and mix. Bring to volume with reagent water and store at $4^\circ\text{C} \pm 2^\circ\text{C}$ in an amber glass bottle. The maximum shelf life is six months or the vendor's expiration date, whichever is earlier

Note: The pyridine barbituric acid may be purchased commercially. Filter 50 ml of the pyridine barbituric acid, and bring up to 250 ml with DI water.

7.1.5. 0.25 N sodium hydroxide: Add 250 mL of 1N NaOH to a 1 liter volumetric flask, and dilute to volume with reagent water.

Note: 0.25 N NaOH may be purchased instead.

7.1.6.

7.2. Standards

7.2.1. Primary Source Cyanide Stock Standard, 1000 mg/L: Add 2.51 g of potassium cyanide (KCN) and 2.0 g of potassium hydroxide (KOH) to a 1000 mL volumetric flask and dilute to volume with reagent water. Mix well and store in glass amber container. Stable for 1-3 months. Additional information can be found in SOP

NC-QA-017.

Note: This stock standard may also be purchased.

Note: Prepared stock standard must be standardized prior to use. See Appendix I (SOP NC-WC-032)

7.2.2. Secondary Source Cyanide Standard, 1000 mg/L: Follow Section 7.2.1 using an alternate source of Potassium Cyanide (KCN).

Note: This stock standard may also be purchased.

Note: Prepared stock standard must be standardized prior to use. See Appendix I (SOP NC-WC-032).

7.2.3. Calibration Standards (Water and Solid Matrices)

7.2.3.1. Pipette the appropriate amount of cyanide standard into 100 mL volumetric and bring to volume with 0.25N NaOH. The low standard must be at, or below, the reporting limit. Prepare weekly.

Concentration CN-Calibration Standards	ML CN-	Final Volume
10 mg/L	1 mL of 1000 mg/L	100 mL Dilution from stock primary and secondary
1.0 mg/L (secondary only)	20 mL of 10 mg/L	200 mL LCS/MS
0.1 mg/L (secondary only)	1 mL of 10 mg/L	100 mL ICV
0.01 mg/L	0.1 mL of 10 mg/L	100 mL MRL check
* 0.2 mg/L	2 mL of 10 mg/L	100 mL Calibrant
0.1 mg/L	1 mL of 10 mg/L	100 mL CCV Solution

*Denotes calibration standards

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Solid samples are not chemically preserved. Water samples are preserved with NaOH to a pH >12. All samples are stored at 4°C ± 2°C in plastic or glass containers.

8.2. The holding time for samples is 14 days from sampling to analysis.

9. QUALITY CONTROL

9.1. Batch Definition

9.1.1. A batch is a group of no greater than 20 samples, excluding QC samples (Laboratory Control Sample (LCS), Method Blank (MB), Matrix Spike/Matrix Spike Duplicate (MS/ MSD)), which are processed similarly with respect to the procedure. All sample setups must be initiated within a 24-hour period from the initial preparation or extraction and without interruption of the process. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.2. Method Blank

9.2.1. One Method Blank (MB) must be processed with each preparation batch. The method blank consists of reagent water or 0.25N NaOH and must contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The Method Blank (MB) is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The Method Blank (MB) must not contain any analyte of interest at, or above, the reporting limit. For Ohio VAP Projects, the Method Blank (MB) must not contain any analyte above the reporting limit.

9.2.2. A Method Blank (MB) consists of 50 mL 0.25N NaOH for Total Cyanide analysis or 50 mL reagent water for Weak Acid Dissociable and Amenable Cyanide analysis must be distilled and analyzed with each analytical batch of samples. See SOP NC-WC-032 for distillation instructions.

9.2.3. Corrective Action for Method Blanks (MBs)

9.2.3.1. If the analyte level in the Method Blank (MB) exceeds the reporting limit for the analytes of interest in the sample, all associated samples are reprepared and re-analyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative.**

9.2.3.2. If there is no analyte greater than the RL in the samples associated with an unacceptable Method Blank (MB), the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

9.3. Laboratory Control Sample (LCS)

9.3.1. One Laboratory Control Sample (LCS) from an independent source must be processed

with each preparation batch. The Laboratory Control Sample (LCS) must be carried through the entire analytical procedure. The Laboratory Control sample (LCS) is used to monitor the accuracy of the analytical process. Ongoing monitoring of the Laboratory Control Sample (LCS) results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- 9.3.2. A midrange Laboratory Control Sample (LCS) consisting of a 0.04 mg/L (2.0 mL of 1.0 mg/L of the secondary source to 50 mL) must be distilled and analyzed with each analytical batch of samples for Total, Amenable, and Weak Acid Dissociable Cyanide analysis. See SOP NC-WC-032 for distillation instruction.

Note: A purchased complex cyanide solution may be used instead as the midrange Laboratory Control Sample (LCS) for Total Cyanide analysis only.

9.3.3. Corrective Action for Laboratory Control Samples (LCSs)

- 9.3.3.1. If any analyte is outside established control limits, the system is out of control and corrective action must occur.
- 9.3.3.2. Corrective action will be re-preparation and re-analysis of the batch unless the client agrees that other corrective action is acceptable. For Ohio VAP samples, the Laboratory Control Samples (LCS) must be redistilled, unless the Laboratory control Sample (LCS) is biased high and the samples are non-detect.
- 9.3.3.3. The only exception is if the Laboratory Control Sample (LCS) recoveries are biased high and the associated sample is ND for the parameter(s) of interest, the batch is acceptable. **This must be addressed in the project narrative.**

- 9.4. Additional information on QC samples can be found in QA Policy QA-003.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

- 9.5.1. One Matrix Spike/Matrix Spike Duplicate (MS/MSD) pair must be processed for each batch. A Matrix Spike (MS) is a field sample to which known concentrations of target analytes have been added. A Matrix Spike Duplicate (MSD) is a second aliquot of the same sample (spiked identically as the Matrix Spike (MS)) prepared and analyzed along with the sample and Matrix Spike (MS). Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of, or in addition to, Matrix Spikes/Matrix Spike Duplicates (MS/MSDs). The Matrix Spike/Matrix Spike Duplicate (MS/MSD) results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the

matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis.

9.5.2. A Matrix Spike/Matrix Spike Duplicate (MS/MSD) consisting of 50 mL or 1.0 g sample and 0.04 mg/L spike (2.0 mL of 1.0 mg/L to 50 mL) must be distilled and analyzed with every batch. See SOP NC-WC-032 for distillation instructions.

9.5.3. Corrective action for Matrix Spikes/Matrix Spike Duplicates (MS/MSDs)

9.5.3.1. If the analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the Laboratory Control Sample (LCS). If the Laboratory Control Sample (LCS) recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the Laboratory Control Sample (LCS) is outside limits, corrective action must be taken. Corrective action must include re-preparation and reanalysis of the batch.

9.5.3.2. If the native analyte concentration in the Matrix Spike/Matrix Spike Duplicate (MS/MSD) exceeds four times the spike level for that analyte, the recovery data is automatically flagged with a “4” in TALS.

9.5.3.3.

9.6. QC Acceptance Criteria

9.6.1. Control limits are established by the laboratory as described in NC-QA-018.

NOTE: Control limits for Laboratory Control Sample (LCS) and Matrix Spike/Matrix Spike Duplicate (MS/MSD) for Method 335.4 are 90% to 110%.

9.6.2. Laboratory control limits are internally generated and updated periodically unless method specified. The latest version is easily accessible via LIMs

9.7. Method Detection Limits (MDLs) and MDL Checks

9.7.1. MDLs and MDL Checks are established by the laboratory as described in SOPs CA-Q-S-006 and NC-QA-021.

9.7.2. MDLs are easily accessible via LIMs .

9.8. Nonconformance and Corrective Action

- 9.8.1. Any deviations from QC procedures must be documented as a nonconformance with applicable cause and corrective action.

10. CALIBRATION AND STANDARDIZATION

10.1. Initial Calibration

- 10.1.1 The instrument is calibrated daily using the 0.2 ppm standard, which is diluted by the instrument into the following concentrations: 0.005, 0.010, 0.025, 0.050, 0.100, 0.200. The calibration is verified by using a midrange ICB. The ICB is composed of the 0.1 ppm secondary standard. The ICB must not vary from the original curve by more than $\pm 10\%$, or recalibration is required. The correlation coefficient of the original curve must be ≥ 0.995 , or recalibration is required. The curve must not be forced through the origin. An ICB sample is analyzed after the ICB. It cannot contain the analyte of interest above the reporting limit or recalibration is required.

10.1.1.1. Linear Regression

The linear fit uses the following functions:

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response
 x = Concentration
 a = Slope
 b = Intercept

10.2. Continuing Calibration

- 10.2.1. The run is checked every ten samples and at the end of the run using a midrange CCV to verify continued linearity. It cannot vary from the original curve by more than $\pm 10\%$, or reanalysis of all samples bracketed by the failing CCV is required. If CCVs continually fail to meet criteria, this would indicate a possible issue with the calibration standard or with the CCV standard solution, and re-preparation and reanalysis of the calibration curve and/or CCV solution is required. The CCV is composed of the 0.1 mg/L primary standard.

10.2.2. System cleanliness is checked every ten samples and at the end of the run using a CCB. It cannot contain the analyte of interest above the reporting limit, or reanalysis of all bracketed samples is required. If CCBs continually fail to meet criteria, immediately stop the analysis and take corrective action. Corrective action can include, but is not limited to, the following: refreshing the CCB solution, recalibration, or instrument maintenance as deemed necessary. The CCB is 0.25N NaOH.

10.3. High and Low Standard

10.3.1. The distillation technique is checked by distilling a high and low standard and comparing the values obtained to the standard curve. The method recommends that the HI/LO standards be compared to the curve with a +/- 10% agreement. Re-analysis must occur if the standards do not meet criteria. The HI/LO standards are evaluated against all applicable batch QC.

10.4 Linear Calibration Range

10.4.1 The Linear Calibration Range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by $\pm 10\%$, linearity must be re-established. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

11. PROCEDURE

11.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure must be completely documented using a Nonconformance Memo and is approved by a Technical Specialist. The Nonconformance Memo must be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described. This is not applicable for Ohio EPA/VAP.

11.3. Sample Preparation

11.3.1. See Cyanide Distillation SOP NC-WC-032.

11.3.1.1. The sample is distilled/refluxed under acidic conditions for one hour. The

released HCN is trapped in 25 mL of 0.25 N NaOH solution. For EPA Method 335.4, reflux for one and a half hours.

11.3.2. Sample Preparation Procedure

11.3.2.1 All Solid Samples: Test each sample for the presence of sulfides using lead acetate paper. If sulfides are present, treat the sample with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution. Avoid a large excess of cadmium carbonate and long contact time in order to minimize loss by complexation or occlusion of cyanide on the precipitated material. **In the case of positive sulfide interference, the Method Blank and LCS must also undergo the sulfide removal treatment.**

Note: Water must be tested prior to distillation. See Cyanide Distillation SOP NC-WC-032.

11.3.3 For DoD work, refer to SOP NC-QA-016 for specific details.

11.4. Sample Analysis

11.4.1. Recommended Instrument Conditions

11.4.1.1. See manufacturer's information for operation instructions.

11.4.1.2. Perform instrument startup.

11.4.1.3. Add reagents to the Konelab reagent wheel.

11.4.1.4. Insert standards and samples to autosampler segments.

11.4.2. Sample Analysis Procedure

11.4.2.1. See manufacturer's information for operating instructions.

11.4.2.2. The correlation coefficient must be > 0.995 to continue. If new standards were not made, then the previous curve may be used if all QC passes criteria.

11.4.2.3. The ICV (from the secondary source) and the ICB is analyzed at the beginning of every run followed by an MRL check. CCVs (from the primary source) and CCBs are analyzed at the end and between every ten samples.

11.4.2.4. Sample distillates higher than the highest calibration standard (0.2 mg/L) must be diluted with 0.25 N NaOH and re-analyzed.

11.4.2.5. Any samples analyzed after a high sample must be re-analyzed if carryover is suspected.

11.4.2.6. If the sample concentration exceeds the working range as defined by the calibration standards, then the sample must be diluted and re-analyzed. Dilutions must target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

11.5. Analytical Documentation

11.5.1. Record all analytical information appropriately in LIMS, including the analytical data from standards, Method Blanks (MBs), Laboratory Control Samples (LCSs), Matrix Spike/Matrix Spike Duplicates (MS/MSDs), and any corrective actions or modifications to the method.

11.5.2. All standards and reagents are logged in the LIMS standards and reagents module. All standards are assigned a unique number for identification.

11.5.3. Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.4. Sample results and associated QC are transferred directly into LIMS from the instrument. Level I and Level II reviews are done in LIMS.

12. DATA ANALYSIS AND CALCULATIONS

$$12.1. \text{ Total Cyanide, mg / L} = \frac{\text{mg / L CN}^-}{\text{mL of sample distilled}} \times 50 \times D$$

$$12.2. \text{ Total Cyanide, mg / kg} = \frac{\text{mg / L CN}^-}{\text{g of sample distilled}} \times 50 \times D$$

$$12.3. \text{ Amenable Cyanide, mg / L} = \text{Total CN}^- (\text{mg / L}) - \text{Chlorinated CN}^- (\text{mg / L})$$

Where:

mg/L = can also be mg/kg

$$D = \text{Dilution Factor} = \frac{\text{Final Volume of Dilution}}{\text{Volume of Sample Distillate Used}}$$

Note: Weak Acid Dissociable Cyanide has the same calculations as Total Cyanide

12.4. Laboratory Control Sample (LCS) Recovery:

$$\frac{\text{Instrument Value}}{0.04(\text{true})} \times 100 = \% \text{ Recovery}$$

Note: The true value may vary by manufacturer or analysis.

12.5. CCV Recovery:

$$\frac{\text{Instrument Value}}{0.1(\text{true})} \times 100 = \% \text{ Recovery}$$

NOTE: CCV recovery must be between 90-110% for data to be acceptable. If CCV recovery is not within these limits, re-analysis is required.

12.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) Recovery for Waters and solids

$$\frac{A - B}{0.040(\text{true})} \times 100 = \% \text{ Recovery}$$

Where:

(MS/MSD)

A = Instrument value Matrix Spike/Matrix Spike Duplicate

B = Sample instrument value

12.7 Additional equations and calculations are listed in the following SOPs: Calibration Curves (General), CA-Q-S-005, and Selection of Calibration Points, CA-T-P-002.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file and corresponding

method detection limit files.

13.2. Training Qualifications

13.2.1. The Group/Team Leader has the responsibility to ensure this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13.2.2. Method validation information (where applicable) in the form of laboratory demonstrations of capabilities is maintained for this method in the laboratory QA files.

14. POLLUTION PREVENTION

14.1. 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". Waste Management

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local laws and 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 Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention".

15.2. Waste Streams Produced by the Method

15.2.1. The waste from Konelab analysis is collected in the waste bucket housed in the instrument. The waste container is emptied at the end of the day in the "Acid Waste" container.

15.2.2. Filter paper contaminated with cadmium sulfide complex. This waste is placed in a container labeled "Solid Waste".

15.2.3. Aqueous rinsates from distillation tube clean up. This waste is collected in the lab and disposed of in a container labeled "Acid Waste".

15.2.4. Standard Waste and High Concentration Samples: This waste is disposed of in the designated container labeled “High Cyanide/Basic Waste.” NO ACID is added to this container.

15.3. Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of TestAmerica. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks followed by annual refresher training.

16. REFERENCES

16.1. References

16.1.1. SW846, Test Methods for Evaluating Solid Waste Method 9012A

16.1.2. EPA 600; Cyanide, Total and Cyanide, Amenable to Chlorination; Methods 335.2, March 1983

16.1.3. EPA 600; Determination of Total Cyanide by Semi-Automated Colorimetry, 335.4, Revision 1.0, August 1993

16.1.4. Standard Methods for the Examination of Water and Wastewater, Eighteenth Edition: Weak and Dissociable Cyanide; Method 4500-CN-E, 4500-CN-I, and 4500-CN-G

16.1.5. [TestAmerica North Canton Quality Assurance Manual \(QAM\)](#), current version

16.1.6. TestAmerica Corporate Environmental Health and Safety Manual, [CW-E-M-001](#), and TestAmerica [North Canton Facility Addendum and Contingency Plan](#), current version

16.1.7. [Corporate Quality Management Plan \(CQMP\)](#), current version

16.1.8. Revision History

Historical File:	Revision 5: 06/24/99	Revision 8.1: 05/30/08
	Revision 6: 06/28/99	Revision 8.2: 12/30/08
	Revision 7: 05/31/01	Revision 8.3: 06/15/10
	Revision 8: 11/08/04	

16.2. Associated SOPs and Policies, latest version

16.2.1. QA Policy, [QA-003](#)

16.2.2. Glassware Washing, [NC-QA-014](#)

16.2.3. Statistical Evaluation of Data and Development of Control Charts, [NC-QA-018](#)

16.2.4. Method Detection Limits and Instrument Detection Limits, [NC-QA-021](#) and [CA-Q-S-006](#)

16.2.5. Supplemental Practices for DoD Project Work, [NC-QA-016](#)

16.2.6. Cyanide Preparation Method, [NC-WC-032](#)

16.2.7. Standards and Reagents, [NC-QA-017](#)

16.2.8. Selection of Calibration Points, [CA-T-P-002](#)

16.2.9. Calibration Curves (General), [CA-Q-S-005](#)

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Reporting limits

17.1.1. The reporting limit (RL) is 0.01 mg/L for waters (50 mL used) and 0.50 mg/kg for solids (1.0 g used). The lowest level of the calibration curve can be used as the reporting limit upon request.

17.1.2. If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

17.2. Method Deviation (9012A/335.2)

17.2.1. Method of Standard Addition is not performed for samples with matrix interference (sulfides).

17.2.2. Method 9012A states that the CCV must be within $\pm 15\%$, or recalibration is required. The laboratory reanalyzes all samples bracketed by CCVs that are outside of $\pm 10\%$, and recalibrates only if deemed necessary by continual failures.



Environmental

DOCUMENT TITLE:

POLYCHLORINATED BIPHENYLS

REFERENCED METHOD:

SW846 8082

SOP ID:

HN-GC-002

REV. NUMBER:

R06

EFFECTIVE DATE:

03/01/2013



POLYCHLORINATED BIPHENYLS

SW846-8082

SOPID: HN-GC-002 Rev. Number: R06 Effective Date: 03/01/2013

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Date: 2/13/13

Laboratory Director – Jeff Glaser

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ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO PROCEDURAL CHANGES HAVE BEEN MADE TO THE SOP SINCE THE APPROVAL DATE ABOVE. THIS SOP IS VALID FOR TWELVE ADDITIONAL MONTHS FROM DATE OF THE LAST SIGNATURE UNLESS INACTIVATED OR REPLACED BY SUBSEQUENT REVISIONS.

Signature _____

Title _____

Date _____

Signature _____

Title _____

Date _____

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Title _____

Date _____



STANDARD OPERATING PROCEDURE

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*POLYCHLORINATED BIPHENYLS*

1) Scope and Applicability

- 1.1 This SOP is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors utilizing a gas chromatograph equipped with electron capture detectors (ECD). The analytical determination of the target analytes listed in Table 1.1 is applicable to this SOP.

Table 1.1

Compound	CAS Registry No.
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5
Aroclor 1262	37324-23-5
Aroclor 1268	11100-14-4

- 1.2 Aroclors are multi-component mixtures of chlorinated biphenyls. 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.
- 1.3 Analyte verification is based on use of a secondary gas chromatographic column to confirm the measurements made with the primary column.

2) Summary of Procedure

- 2.1 A measured volume or weight of sample (approximately 1 L for liquids or 15 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.
- 2.2 Aqueous samples are extracted at neutral pH with methylene chloride using Method 3510C (separatory funnel). Solid samples are extracted with a hexane/acetone mixture using Method 3540 (Soxhlet), Method 3541 (Automated Soxhlet), or Method 3550 (ultrasonic extraction). The extraction procedures use a hexane solvent exchange (if necessary) in preparation of the final extract for analysis by GC/ECD.
- 2.3 Sample extracts may be subjected to a sulfuric acid cleanup (Method 3665). This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides. Therefore, Method 8082 is not applicable to the analysis of those compounds.
- 2.4 After cleanup, the extract is analyzed by injecting a 0.5- μ L aliquot into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD).

3) Definitions



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- 3.1 GC/ECD = Gas Chromatograph / Electron Capture Detector
- 3.2 Organic Free Water: Deionized (DI) reagent water meeting purity characteristics of ASTM Type II laboratory distilled water (daily conductivity <1.0 umhos/cm). For additional purification before use, the DI water is passed through an activated carbon filter.
- 3.3 Laboratory Control Sample (LCS): A known matrix spiked with compound(s) representative of the target analytes and used to evaluate/document laboratory method performance.
- 3.4 Matrix: The component or substrate (e.g., surface water, groundwater, soil) containing the analyte(s) of interest.
- 3.5 Matrix Spike (MS): An aliquot of sample spiked with a known concentration of target analyte(s) prior to sample extraction and processing. The MS is used to evaluate bias of a method in a given sample matrix.
- 3.6 Matrix Spike Duplicate (MSD): A duplicate sample spiked with identical concentrations of target analyte(s) prior to sample extraction and processing. The MS/MSD pair is used to assess the precision and bias of a method in a given sample matrix.
- 3.7 Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document the presence/absence of contamination as a result of the analytical process.
- 3.8 Standard Curve: A plot of known analyte concentrations (standards) versus the instrument response.
- 3.9 Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.
- 3.10 CAR: Corrective Action Report (refer to SOP HN-QS-003, current revision).

4) Health and Safety Warnings

4.1 Lab Safety

- 4.1.1 Due to various hazards in the laboratory, safety glasses, disposable gloves, and laboratory coats or aprons must be worn when working with unknown samples. In addition, heavy-duty gloves and a face shield are recommended when dealing with toxic, caustic, and/or flammable chemicals.
- 4.1.2 The toxicity or carcinogenicity of each reagent used has not been precisely defined. However, each chemical used must be treated as a potential health hazard and exposure reduced to the lowest possible level. The laboratory maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets (MSDS) is available to all personnel involved in these analyses.

4.2 Waste Disposal

- 4.2.1 Procedures for sample disposal are documented in SOP HN-SAF-001, *Waste Disposal Procedures*.



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4.2.2 Samples must be disposed according to Federal, State, and local regulations.

4.3 Pollution Prevention

4.3.1 The quantities of chemicals purchased, when possible, must be based on the expected usage during its shelf life.

4.3.2 Standards and reagents must be prepared in volumes consistent with laboratory use to minimize the volume of expired standards or reagents to be disposed.

5) Cautions

5.1 Electron capture detectors are sensitive to the presence of chlorinated compounds. Exposure of the detectors to extraneous chlorinated sources, such as methylene chloride, must be avoided.

5.2 Routine preventative maintenance must be performed as scheduled and documented to assure optimum instrument performance. Refer to HN- EQ-004 for additional information.

6) Interferences

6.1 Interferences co-extracted from the samples will vary considerably from matrix to matrix. 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. Sources of interference in this method can be grouped into three broad categories.

6.1.1 Contaminated solvents, reagents, or sample processing hardware.

6.1.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.

6.1.3 Compounds extracted from the sample matrix to which the detector will respond.

6.2 Interferences by phthalate esters introduced during sample preparation can bias PCB peak pattern determinations.

6.2.1 Avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination can best minimize interferences from phthalate esters.

6.2.2 Exhaustive cleanup of solvents, reagents and glassware may be required to eliminate background phthalate ester contamination. These materials can be removed through the use of Method 3665 (sulfuric acid cleanup).

6.3 Clean all glassware as soon as possible after use by rinsing with the last solvent used. After rinsing, wash all glassware utilizing the procedures documented in SOP HN-GEN-003 (glassware cleaning).

7) Personnel Qualifications and Responsibilities

7.1 General Responsibilities - This method is restricted to use by or under the supervision of analysts experienced in the method.

7.2 Analyst - It is the responsibility of the analyst(s) to:



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- 7.2.1 Produce contractually compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.
- 7.2.2 Complete the required demonstration of proficiency prior to performing this procedure independently.
- 7.2.3 Create and populate a data entry batch in Omega for review by the Supervisor (or designee).
- 7.3 Section Supervisor - It is the responsibility of the section supervisor to:
 - 7.3.1 Ensure that all analysts have the technical ability and have received adequate training required to perform this procedure.
 - 7.3.2 Ensure analysts have completed the required demonstration of proficiency prior to performing this procedure without supervision.
 - 7.3.3 Produce contractually compliant data that meets all quality requirements using this procedure and the Data Reduction, Review and Validation SOP.
- 7.4 Project Manager - It is the responsibility of the Project Manager to ensure that all contractual requirements for a client requiring this procedure are understood prior to initiating this procedure for a given set of samples.

8) Sample Collection, Handling, and Preservation

- 8.1 All samples must be iced or refrigerated at 4°C (+/- 2 °C) from the time of collection until extraction. Refer to Table 8.1 for sample containers, sample preservation and sample holding time information.

TABLE 8.1 - SEMIVOLATILE ORGANICS / ORGANOCHLORINE PESTICIDES/ PCBs AND HERBICIDES			
Sample Matrix	Container	Preservative	Holding Time
Concentrated Waste Samples	125-ml widemouth glass with Teflon lined lid.	None	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.
Aqueous Samples With No Residual Chlorine Present	1-gal., 2 x 0.5-gal., or 4 x 1-L, amber glass container with Teflon-lined lid.	Cool to 4°C	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Aqueous Samples WITH Residual Chlorine Present	1-gal, 2 x 0.5-gal., or 4 x 1-L, amber glass container with Teflon-lined lid.	Add 3-ml 10% sodium thio-sulfate solution per gallon (0.008%). Addition of so-dium thiosulfate solution to sample container may be per-formed in the laboratory prior to field use. Cool to 4°C.	Samples extracted within 7 days and extracts analyzed within 40 days following extraction.
Solid Samples (e.g. soils, sediments, sludges, ash)	250-ml wide mouth glass container with Teflon-lined lid	Cool to 4°C	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.
Wipes	2-oz wide mouth glass container with Teflon-lined lid	Cool to 4°C	Samples extracted within 14 days and extracts analyzed within 40 days following extraction.

9) Equipment and Supplies

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- 9.1 Gas chromatograph – Agilent 6890 (or equivalent) GC equipped with electron capture detectors (ECDs).
- 9.2 GC columns:
 - 9.2.1 Primary: 30.0m x 0.25mm ID x 0.25um Rtx-CLPesticides (Restek cat.# 11123)
 - 9.2.2 Secondary: 30.0m x 0.25mm ID x 0.20 um Rtx-CLPesticides2 (Restek cat.# 11323)
 - 9.2.3 5m x 0.25mm ID Siltek Deactivated Guard Column
- 9.3 Syringes - 10ul, 0.1ml, 0.5ml & 1.0ml
- 9.4 Volumetric Flasks, class A, assorted sizes
- 9.5 2-ml clear auto-sampler vials with screw cap closures lined with PTFE (Teflon).

10) Standards and Reagents

- 10.1 n-Hexane and Acetone - reagent grade or higher
- 10.2 Solvents used in the extraction and cleanup procedures (see appropriate 3500 and 3600 SOPs) include n-hexane and methylene chloride. Acetone or toluene may also be required. All solvents must be reagent grade or higher.
- 10.3 Aroclor Stock Standards in hexane @ 100 ug/ml (Restek or equivalent)
 - 10.3.1 Aroclor 1221 @ 100 µg/ml in hexane
 - 10.3.2 Aroclor 1232 @ 100 µg/ml in hexane
 - 10.3.3 Aroclor 1242 @ 100 µg/ml in hexane
 - 10.3.4 Aroclor 1248 @ 100 µg/ml in hexane
 - 10.3.5 Aroclor 1254 @ 100 µg/ml in hexane
 - 10.3.6 Aroclor 1262 @ 100 µg/ml in hexane
 - 10.3.7 Aroclor 1268 @ 100 µg/ml in hexane
- 10.4 Aroclor 1016/1260 Mix in hexane @ 1000 ug/ml (Restek #32039 or equivalent)
- 10.5 Pesticide Surrogate Standard Spiking Solution in acetone @ 200 ug/ml, (Ultra ISM-320 or equivalent)
- 10.6 Calibration Working Stock @ 10 ug/ml Aroclor and 0.20 ug/ml Surrogate
 - 10.6.1 Add approximately 8 ml n-hexane to a 10 ml Class A volumetric flask.
 - 10.6.2 Add 100 ul of the Aroclor 1016/1260 stock (Section 10.4)
 - 10.6.3 Add 10 ul of the Surrogate stock (Section 10.5)
 - 10.6.4 Bring to volume with n-hexane and mix
 - 10.6.5 Transfer to a clean appropriately labeled amber container
 - 10.6.6 Replace after 6 months or if degradation is noted. The expiration date may not exceed that of any parent stock.
- 10.7 Initial Calibration Standards, (Aroclor 1016/1260 w/surrogates):
 - 10.7.1 Using the appropriate syringe, inject the amounts documented in Table 10.7.1 of the Calibration Working Stock (Section 10.6) into a clean appropriately labeled 2 ml amber vial containing the designated amount of reagent grade n-Hexane.



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- 10.7.2 Mix and store refrigerated.
- 10.7.3 Replace after 6 months or if degradation is noted. The expiration date may not exceed that of any parent stock.

Table 10.7.1	Initial Calibration Standards - Concentration (ng/ml)						
ul of Calibration Working Stock	10ul	25ul	50ul	100ul	200ul	300ul	500ul
ul of n-Hexane	990ul	975ul	950ul	900ul	800ul	700ul	500ul
Final Volume	1 ml	1 ml	1 ml	1 ml	1 ml	1 ml	1 ml
Compound Name	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
Aroclor 1016/1260, ppb	100	250	500	1000	2000	3000	5000
Tetrachloro-meta-xylene (surrogate), ppb	2	5	10	20	40	60	100
Decachlorobiphenyl (surrogate), ppb	2	5	10	20	40	60	100

10.8 Single Point Calibration Standards @ 5.0 ug/ml (non - 1016/1260)

- 10.8.1 Using the appropriate syringe, inject 50 ul of the appropriate Aroclor Stock @ 100 ug/ml (Section 10.3) into a 2 ml amber vial containing 950ul of reagent grade n-Hexane.
- 10.8.2 Mix and store refrigerated.
- 10.8.3 Replace after 6 months or if degradation is noted. The expiration date may not exceed that of its parent compound.

10.9 Pesticide/PCB Surrogate Spiking Mix @ 1.0 ug/mL:

- 10.9.1 Add approximately 80 ml of hexane to a 100 ml Class A volumetric flask.
- 10.9.2 Add 500 ul of the stock Surrogate mix (Section 10.5)
- 10.9.3 Bring to volume with hexane and mix
- 10.9.4 Transfer to a clean appropriately labeled amber bottle
- 10.9.5 Replace after 6 months or if degradation is noted. The expiration date may not exceed that of the parent stock.

10.10 Stock PCB (1016/1260) LCS/MS Spike @ 1000 ug/ml: (Ultra PPM-8082)

10.10.1 PCB LSC/MS Water Spiking Mix @ 5 ug/ml:

- 10.10.1.1 Add approximately 95 ml of n-hexane to a 100 ml Class A volumetric flask,
- 10.10.1.2 Add 500 ul of the stock PCB Spike mix (Section 10.10)
- 10.10.1.3 Bring to volume with n-hexane
- 10.10.1.4 Transfer to a clean appropriately labeled amber bottle and store refrigerated.
- 10.10.1.5 Replace after 6 months or if degradation is noted. The expiration date may not exceed that of the parent stock.

10.10.2 PCB LCS/MS Soil Spiking Mix @ 50 ug/ml

Refer to Section 10.10.1

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- 11.3.3 If the RSD for each analyte is < 15%, then the response of the instrument is considered linear and the mean calibration factor can be used to quantitate sample results. If the RSD is greater than 15%, then linearity through the origin cannot be assumed. The analyst must use a linear calibration curve or a non-linear calibration model (e.g., a polynomial equation) for quantitation.
- 11.3.4 For a linear calibration curve ($y = ax + b$), the analyst should not force the line through the origin, but leave the intercept calculated.

11.3.4.1 For an acceptable calibration curve, the coefficient of determination (COD) must be ≥ 0.995 .

- 11.3.5 If the approaches described above have not met the acceptance criteria, a non-linear calibration model may be employed. The quadratic (second order) model requires six standards.

11.3.5.1 $Y = ax^2 + bx + c$

11.3.5.2 For an acceptable non-linear calibration, the coefficient of the determination (COD) must be ≥ 0.995 .

11.3.6 Retention Time (RT) Windows

- 11.3.6.1 Record the retention time of each peak in the peak pattern.
- 11.3.6.2 Calculate the mean RT and standard deviation (SD) of each peak
- 11.3.6.3 The RT Window for each peak is defined at ± 3 times the SD around the mean RT.
- 11.3.6.4 If the SD of the retention time is 0, a default value of 0.03 minutes should be used to define the window.

11.4 Initial Calibration Verification

- 11.4.1 Verify each new Initial Calibration using a second source standard at or below the midpoint of the curve.
- 11.4.2 Agreement with the new curve must be ± 15 percent of the true value of the second source standard.

11.5 Continuing Calibration Verification

- 11.5.1 Utilizing a mid-level calibration standard, verify instrument calibration prior to any sample analyses, at intervals of not less than once every twenty samples, and at the end of the analytical sequence.
- 11.5.2 The calibration factor for each analyte must not exceed a ± 15 percent difference from the mean calibration factor calculated for the initial calibration. If a non-linear model has been employed for the initial calibration, % drift must be $\pm 15\%$. Refer to section 15 for calculation of % drift.
- 11.5.3 If the calibration does not meet the $\pm 15\%$ limit, check the instrument operating conditions, perform any needed maintenance, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within $\pm 15\%$, a new initial calibration must be prepared.
- 11.5.4 Compare the retention time of each analyte in the calibration standard with



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the retention time window established in Section 11.3.5. Each analyte in each standard must fall within its respective retention time window. If not, the gas chromatographic system must either be adjusted so that a second analysis of the standard achieves acceptance criteria or a new initial calibration must be performed and new retention time windows established.

12) Sample Preparation/Analysis

12.1 Sample Preparation

12.1.1 Water samples are prepared by separatory funnel extraction, method SW 3510, HN-EXT-001.

12.1.2 Soils:

12.1.2.1 Soil samples are extracted by method SW 3540 (soxhlet) HN-EXT-002.

12.1.2.2 Alternatively, soil samples can be extracted using SW 3550B (ultrasonic).

12.1.3 Wipes:

12.1.3.1 Add 1 ml of the PCB/Pest working surrogate standard to the 2 oz container holding the wipe sample.

12.1.3.2 Add 10 ml of reagent grade (or higher) hexane.

12.1.3.3 Sonicate for a period of no less than 10 minutes.

12.1.3.4 Transfer a portion of the hexane to an appropriately labeled container and analyze per Section 12.2.

12.1.3.5 Report PCB content in units of $\mu\text{g/wipe}$.

12.2 Sample Analysis

12.2.1 Operating Conditions

12.2.1.1 See Section 11, Table 11.1.



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- 12.3 Qualitative identifications of target analytes are made by examination of the sample chromatograms and comparison of sample peak patterns versus the peak patterns established from individual standards
- 12.4 Quantitative results are determined for each identified Aroclor using the external calibration procedure. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze.
- 12.5 Sample analysis must be bracketed with acceptable calibration verification standards. Should a calibration verification standard fail to meet QC criteria, all samples that were injected after the last acceptable standard must be re-analyzed.
- 12.6 Multi-level standards are highly recommended during the analytical sequence to ensure that detector response remains stable over the calibration range.
- 12.7 Sample injections may continue for as long as the calibration verification standards meet instrument QC requirements.
- 12.8 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their established retention time windows, the problem must be corrected and all associated sample extracts re-analyzed.
- 12.9 If compound identification or quantitation cannot be completed due to matrix interferences (e.g., broad, rounded peaks or ill-defined baselines) cleanup of the extract or replacement of the capillary column is warranted.
- 12.10 Qualitative identification
 - 12.10.1 Identification of PCBs is based on the agreement of peak pattern, peak pattern retention time, and peak area ratios in the sample chromatogram with those established through the analysis of standards.
 - 12.10.2 Tentative identification of an Aroclor peak pattern from a sample extract must correlate with the pattern, retention time, and peak area ratios established from the respective standard. Tentative identification must be confirmed using a second GC column of dissimilar stationary phase.
 - 12.10.3 When samples are analyzed from a source known to contain specific Aroclors and for which site history is available, the results from a single-column analysis may be confirmed on the basis of a clearly recognizable Aroclor pattern. This approach is not applicable for samples from unknown or unfamiliar sources or for samples that appear to contain mixtures of Aroclors.
- 12.11 PCB Quantitation (as Aroclor)
 - 12.11.1 The quantitation of PCB Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.
 - 12.11.1.1 Aroclor identification must address:
 - 12.11.1.1.1 Presence of the established peak pattern,
 - 12.11.1.1.2 Elution at the established retention time, and
 - 12.11.1.1.3 Appropriate peak area ratios.



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12.11.1.2 If matrix interference precludes a positive identification, the extract should be processed through additional clean up procedures and/or diluted and re-analyzed until the criteria specified in 12.11.1.1.1 through 12.11.1.1.3 are achieved.

12.11.2 Use the individual Aroclor standards (not the Aroclor 1016/1260 mixture) to determine the peak pattern for Aroclors 1221, 1232, 1242, 1248, 1254, 1262, or 1268. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

12.11.3 Calculate the amount of Aroclor using the individual calibration factor for each of the characteristic peaks. A concentration is determined using each of these characteristic peaks and then averaged to determine the concentration of the Aroclor.

12.11.3.1 If matrix interference precludes the use of all peaks in the pattern for quantitation, a subset of peaks may be used at the analyst's discretion.

12.11.3.2 The subset must contain, at a minimum, three representative peaks.

12.11.3.3 Initial calibration parameters must be adjusted accordingly to reflect use of the subset.

12.11.4 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 such instances, analyst judgment and experience must be utilized for the qualitative determination.

13) Troubleshooting

13.1 Refer to Agilent 6890 GC hardware manual for specific technical guidance.

14) Data Acquisition

14.1 Instrument operation and data collection utilizes HP ChemStation with Enviroquant data acquisition software.

14.2 Enviroquant data processing software converts the acquired signal information into final results.

15) Calculation, and Data Reduction Requirements

15.1 Calibration Factor (CF) and calibration RSD calculations:

15.1.1 Calibration Factor and Mean Calibration Factor:

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

15.1.1.1



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$$15.1.1.2 \quad \text{Mean CF} = \overline{\text{CF}} = \frac{\sum_{i=1}^n \text{CF}_i}{n}$$

where: n is the number of standards analyzed.

15.1.2 Standard Deviation (SD) and RSD:

$$\text{SD} = \sqrt{\frac{\sum_{i=1}^n (\text{CF}_i - \overline{\text{CF}})^2}{n-1}} \quad \text{RSD} = \frac{\text{SD}}{\overline{\text{CF}}} \times 100$$

15.2 Calculation of Linear Regression Correlation Coefficient, r

$$r = \frac{\sum XY - \frac{\sum X \sum Y}{n}}{\sqrt{(\sum X^2 - \frac{(\sum X)^2}{n})(\sum Y^2 - \frac{(\sum Y)^2}{n})}}$$

Where:

X = individual values for independent variable

Y = individual values for dependent variable

n = number of pairs of data.

df = n-2

15.3 Calculation of % difference (using the calibration factors):

$$15.3.1 \quad \% \text{ Difference} = [(\text{CF} - \text{mean CF}) \times 100] / \text{mean CF}$$

where:

CF = the calibration factor from the CCV and

mean CF = the mean calibration factor from the initial calibration

15.4 Calculation of % drift (linear and non-linear regression) uses the following formula:

$$15.4.1 \quad \% \text{ Drift} = \frac{[(\text{Calculated Conc.} - \text{Theoretical Conc.}) \times 100]}{\text{Theoretical Conc.}}$$

15.5 Dual Column Confirmation RPD: When results are confirmed using a second GC column of dissimilar stationary phase, the analyst evaluates the agreement between the quantitative results on both the primary and secondary columns. If the RPD is > 40%, the higher result is reported unless specified otherwise by the project plan. Calculate the relative percent difference of the results using the formula below.

$$15.5.1 \quad \text{RPD} = [R_1 - R_2] * 100 / ((R_1 + R_2) / 2)$$

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Where: R_1 and R_2 are the results on the two columns. The difference result for $[R_1 - R_2]$ in the equation above is taken as the absolute value of the difference. Therefore, the RPD is always a positive.

15.6 Sample Quantitation using External calibration, aqueous samples:

$$\text{Concentration (ug/L)} = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(V_s)}$$

where:

- A_x = Area (or height of the peak) for the analyte in the sample.
 V_t = Total volume of the concentrated extract (ml).
 D = Dilution factor (if sample/extract was diluted prior to analysis)
 CF = Mean calibration factor from the initial calibration (area/ng).
 V_i = Volume of the extract injected (ml).
 V_s = Volume of the aqueous sample extracted in L.

15.7 Sample Quantitation using External calibration, solid samples:

$$\text{Concentration (ug/kg)} = \frac{(A_x)(V_t)(D)}{(CF)(V_i)(W_s)}$$

where:

- A_x = Area (or height of the peak) for the analyte in the sample.
 V_t = Total volume of the concentrated extract (ml).
 D = Dilution factor (if sample/extract was diluted prior to analysis)
 CF = Mean calibration factor from the initial calibration (area/ng).
 V_i = Volume of the extract injected (ml).
 W_s = Weight of sample extracted in kg.

15.8 QC Calculations: Calculate the percent recovery for surrogates and for various QC samples (MS, MSD, LCS) according to the following equations:

- 15.8.1 Surrogate Recovery: Sample, matrix spike/matrix spike duplicate, duplicate, and blank samples are all spiked with surrogates prior to extraction. Surrogate percent recovery is calculated as follows:

$$\%R = \frac{\text{SurrSR}}{\text{SurrSA}} \times 100$$

where:

- SurrSR = Surrogate Spiked Sample Result ($\mu\text{g/L}$ or $\mu\text{g/kg}$).
SurrSA = Surrogate Spike Amount Added ($\mu\text{g/L}$ or $\mu\text{g/kg}$).

15.8.2 % Recovery, %R (for MS and MSD Samples)



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$$\%R = \frac{(SSR - SR)}{SA} \times 100$$

where:

SSR = Spiked Sample Result ($\mu\text{g/L}$ or $\mu\text{g/kg}$).

SR = Sample Result (unspiked).

SA = Spike Amount Added ($\mu\text{g/L}$ or $\mu\text{g/kg}$).

15.8.3 % Recovery, %R (for standards and LCS)

$$\%R = \frac{SSR}{SA} \times 100$$

where:

SSR = Spiked Sample Result ($\mu\text{g/L}$ or $\mu\text{g/kg}$).

SA = Spike Amount Added ($\mu\text{g/L}$ or $\mu\text{g/kg}$).

15.8.4 % RPD (for precision or replication evaluation)

$$\%RPD = \frac{|SR_1 - SR_2|}{\frac{1}{2}(SR_1 + SR_2)} \times 100$$

where:

SR₁ = Sample result for replicate 1.

SR₂ = Sample result for replicate 2.

16) Quality Control, Data Assessment and Corrective Action

16.1 Initial Calibration:

16.1.1 Frequency: A new curve must be generated when the ICV or CCV criteria are not met, after major instrument maintenance, or changes in operating conditions

16.1.2 Acceptance Criteria:

16.1.2.1 Curve must contain 5 points minimally for the 1016/1260 standard.

16.1.2.2 The mean RSD must be $\leq 15\%$, or

16.1.2.3 Establish calibration by least squares regression, or

16.1.2.3.1 COD must ≥ 0.995 .

16.1.2.4 Establish calibration by quadratic (second order) model



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- 16.1.2.4.1 Six standards minimally must be used, and
- 16.1.2.4.2 Coefficient of determination (COD) must be ≥ 0.995 .

16.1.3 Curve Failure Corrective Action:

- 16.1.3.1 Verify standard integrity, perform any necessary instrument maintenance, and repeat calibration process.
- 16.1.3.2 All samples associated with a failed initial calibration curve must be reanalyzed prior to reporting. If reanalysis cannot be completed, all associated sample results must be flagged as "unusable" and narrated.

16.2 Initial Calibration Verification (ICV):

- 16.2.1 Perform evaluation each time a new curve is generated.
- 16.2.2 Verification must be completed against a second source standard. If an alternative supplier is not available, a different lot number must be used.
- 16.2.3 Agreement between the curve and the ICV results must meet accuracy performance criteria as outlined in the applicable LIMS test code.
- 16.2.4 If the ICV fails to achieve acceptance criteria, evaluate standard integrity and/or perform any needed system maintenance. If a subsequent ICV analysis cannot achieve acceptance criteria, prepare new standards and/or generate new curve.
- 16.2.5 All samples associated with a failed ICV must be reanalyzed prior to reporting. If reanalysis cannot be completed, all associated sample results must be flagged as "unusable" and narrated.

16.3 Continuing Calibration Verification (CCV):

- 16.3.1 The CCV must be analyzed at the beginning of each daily sequence, minimally after every 20 samples, and at the end of the sequence.
- 16.3.2 All analytes must meet accuracy performance criteria as outlined in the applicable LIMS test code.
- 16.3.3 If the calibration does not meet the criteria, perform any necessary maintenance and re-analyze the standard. If the subsequent CCV fails to achieve acceptance criteria, prepare a new calibration curve.
- 16.3.4 All samples associated with a failed CCV must be reanalyzed prior to reporting. If reanalysis cannot be completed, all associated sample results must be flagged as "estimated" and narrated.

16.4 Retention Time (RT) Window:

- 16.4.1 Calculate new RT windows with each new curve.
- 16.4.2 The RT window must be set at ± 3 times the SD relative to the mean RT for each analyte.
- 16.4.3 Peak patterns for standards and QC samples must fall within the documented RT window. (For field samples, analyst judgment may be substituted in situations involving chromatographic matrix interference.)
- 16.4.4 If RT acceptance criteria are not achieved, perform any necessary instrument maintenance and repeat the analysis. If the subsequent analysis fails to achieve acceptance criteria, perform a new initial calibration and establish updated RT windows.



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16.5 Method Blank:

- 16.5.1 A method blank must be processed at a frequency of one per analytical batch of 20 or less samples. If the method blank indicates contamination, process an instrument blank to document instrument cleanliness.
- 16.5.2 Analytes of interest should be less than $\frac{1}{2}$ the MQL and must be less than the MQL.
 - 16.5.2.1 Other approved QA program requirements must be followed when the acceptable blank contamination specified in the approved quality assurance project plan differs from the above.
 - 16.5.2.2 If blank contamination is present, the blank may be considered valid if the analytes of interest are less than 5% of the regulatory limit associated with an analyte or analytes of interest are less than 5% of the sample result for the same analyte, whichever is greater.
- 16.5.3 If the method blank results do not meet acceptance criteria, the contamination source(s) must be eliminated and all associated samples re-extracted. If samples cannot be re-extracted because of insufficient sample or other similar circumstances, a corrective action report must be initiated and issued to project management and to QA. The CAR must be detailed enough for preparation of the project narrative, and all appropriate data flags must be entered into the LIMS for the final report preparation. Data reported with an associated contaminated method blank must be flagged with a "B".

16.6 Laboratory Control Sample (LCS):

- 16.6.1 The LCS must be processed with each batch of 20 or less samples utilizing a clean matrix.
- 16.6.2 LCS recovery must meet accuracy performance criteria as outlined in the applicable LIMS test code.
- 16.6.3 If the LCS recoveries for the compounds of interest do not meet acceptance criteria, the sample batch must be re-extracted. If reprocessing it is not possible due to lack of sample or expired hold time, report (narrate) the variance to the client and flag the associated data as "estimated".

16.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

- 16.7.1 Samples should be spiked with the Aroclor 1016/1260 mixture.
- 16.7.2 The MS/MSD should be processed with each batch of 20 samples or less (assuming sufficient sample volume).
- 16.7.3 MS/MSD recovery must meet accuracy and precision performance criteria as outlined in the applicable LIMS test code.
- 16.7.4 If the MS/MSD recoveries are outside acceptance criteria, the deviation may be related to matrix effects. In such instances, the LCS and surrogate recoveries must be carefully evaluated to determine if matrix interference is present or if method performance is poor. (Note that the MS/MSD are used to evaluate the matrix effect, not to control the analytical process.) If matrix interference is suspected, re-extraction is not necessary. If systemic error is suspected, all associated samples must be re-extracted.





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16.8 Surrogates

- 16.8.1 Surrogates must be added to all sample. The recoveries must be evaluated for all samples and QC samples.
- 16.8.2 Surrogate recovery for interference free matrices (MB/LCS) must fall within 50% - 130% for waters and 40%-140% for soils. Surrogate recovery for field samples should fall within 40% - 140% for both waters and soils.
- 16.8.3 If the surrogate recoveries do not meet acceptance criteria:
 - 16.8.3.1 Check for possible errors in the calculations or surrogate solutions. If errors are found, recalculate the data accordingly.
 - 16.8.3.2 Examine chromatograms for interfering peaks and proper integration.
 - 16.8.3.3 If no instrument problem is found, the sample should be re-extracted and re-analyzed. If, upon re-analysis, the recovery is not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the re-analysis data to the data user.
 - 16.8.3.4 If the holding time for the method has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem.

17) Data Records Management

- 17.1 All data must be retained for a period of not less than 7 years and electronic records shall be retained for a period of not less than 7 years.
- 17.2 Hard copy documentation must be maintained for standard/chemical tracking, extraction procedures, instrument maintenance, and run logs.
- 17.3 The primary analyst must review raw data after analysis and complete the data checklist. Any manual integrations or deletions must be dated and initialed by the analyst.
- 17.4 Instrument hardcopies must be maintained in daily batch folders that are instrument specific. The folder shall contain the associated sequence log, CCV summary sheet, all raw data w/quantitation report, and data checklist.
- 17.5 Each batch must be peer reviewed by the department supervisor (or designee) prior to final reporting in the laboratory information management system (LIMS).
- 17.6 Pending data review and verification, all batch folders must be stored systemically in the instrument work area. After three months (or as defined by storage limitations), data must be transferred to the QA department for archival.
- 17.7 All data acquisition information must be stored on the computer hard drive and archived to CD format on a monthly basis.

18) Quality Assurance and Quality Control



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- 18.1 Logbooks must be reviewed monthly by the department supervisor.
- 18.2 Logbooks must be reviewed quarterly by the QA Staff.
- 18.3 The QA staff must conduct periodic audits to evaluate compliance with this SOP.

19) Contingencies for Handling Out of Control Data

- 19.1 When QC failures occur, the source of the QC failure must be determined, corrected, and sample reanalysis carried out whenever possible.
- 19.2 When sample analysis cannot be repeated due to sample unavailability or holding time issues, data associated with failed QC data must be appropriately flagged and narrated.
- 19.3 All deviations from documented acceptance criteria must be documented on the data checklist and, if applicable, a Non-Conformance/Corrective Action Report (NC/CA) submitted to the QA Manager via the NC/CA database.

20) Method Performance

- 20.1 Demonstration of Proficiency:
 - 20.1.1 Each analyst must demonstrate initial proficiency with sample preparation and/or determination by generating 4 sets of data of acceptable accuracy and precision for target analytes in a clean matrix.
 - 20.1.2 Each analyst must demonstrate ongoing proficiency annually with sample preparation and/or determination by generating 4 sets of data of acceptable accuracy and precision for target analytes in a clean matrix, or by acceptable PE studies.
- 20.2 Method Detection Limits (MDLs) must be determined on each instrument on an annual basis (at minimum), and whenever major modifications are performed.

21) Summary of Changes

Table 21.1 Summary of Changes

Revision Number	Effective Date	Document Editor	Description of Changes
R05	9/1/12	CES	Formatting
R06	2/1/13	DWD	Addition of Wipe Procedure

22) References and Related Documents



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- 22.1 U.S. Environmental Protection Agency, "Method 8082 Polychlorinated Biphenyls by Gas Chromatography", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Update III, June 13, 1997.
- 22.2 U.S. Environmental Protection Agency, "Method 8000B Determinative Chromatographic Separations", Test Methods for Evaluating Solid Waste Physical/Chemical Methods, Update III, June 13, 1997.
- 22.3 U.S. Army Corps of Engineers, Shell Document, EM 200-1-3, February 2001.
- 22.4 ALS Environmental Quality Assurance Manual, Rev 6.0 (or most current)
- 22.5 Table 20.1 - MDL/MQL
- 22.6 Table 20.2 - LCS Acceptance Criteria
- 22.7 Table 20.3 - MS/MSD Acceptance Criteria
- 22.8 Table 20.4 - QA Criteria Summary

Table 20.1 - Current Aroclor MDLs and MQLs, at time of SOP revision. MDLs are determined annually at a minimum, and are subject to change.

Analyte - water matrix	MDL	MQL	Analyte - solid/soil matrix	MDL	MQL
	µg/L	µg/L		µg/Kg	µg/Kg
Aroclor 1016	0.067	0.25	Aroclor 1016	35.59	40.0
Aroclor 1221	0.067	0.25	Aroclor 1221	35.59	40.0
Aroclor 1032	0.067	0.25	Aroclor 1032	35.59	40.0
Aroclor 1242	0.067	0.25	Aroclor 1242	35.59	40.0
Aroclor 1248	0.067	0.25	Aroclor 1248	35.59	40.0
Aroclor 1254	0.067	0.25	Aroclor 1254	11.16	40.0
Aroclor 1260	0.067	0.25	Aroclor 1260	11.16	40.0

Table 20.2 - SW 8082 LCS Recovery Limits.

Analyte - Water Matrix	Low	High	Analyte - Soil Matrix	Low	High
Aroclor 1016	50	130	Aroclor 1016	50	130
Aroclor 1260	50	130	Aroclor 1260	50	130
Decachlorobiphenyl	50	130	Decachlorobiphenyl	40	140
Tetrachloro-m-xylene	25	140	Tetrachloro-m-xylene	45	124

Table 20.3 - SW 8082 MS/MSD Recovery Limits.

Analyte - Water Matrix	Low	High	RPD	Analyte - Soil Matrix	Low	High	RPD
Aroclor 1016	40	140	50	Aroclor 1016	40	140	50
Aroclor 1260	40	140	50	Aroclor 1260	40	140	50
Decachlorobiphenyl	40	140	50	Decachlorobiphenyl	40	140	50
Tetrachloro-m-xylene	25	140	50	Tetrachloro-m-xylene	45	124	50

Table 20.4 - Summary of Calibration and QC Procedures for Method SW8082



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QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action
Eight-point initial calibration.	Initial calibration prior to sample analysis.	Linear - mean RSD for all analytes <15%; or Linear - least squares regression $r > 0.995$ (six points required)	Correct problem then repeat initial calibration.
Initial calibration verification for PCB 1016/1260 mix.	Once per five-point initial calibration. Required second source standard.	Mix within $\pm 15\%$ of expected value.	Correct problem then repeat initial calibration.
Retention time window calculated for PCB 1016/1260 mix.	Each initial calibration and calibration verifications.	± 3 times standard deviation for each analyte relative to mean RT	Correct problem then reanalyze all samples analyzed since the last retention time check.
Continuing calibration verification for PCB 1016/1260 mix.	Daily, before sample analysis, after every 20 samples, and end of sequence.	All analytes within $\pm 15\%$ of expected value.	Correct problem then repeat initial calibration.
Demonstrate ability to generate acceptable accuracy and precision using four replicate LCS.	Once per analyst.	QC acceptance criteria, Table 20.2.	Recalculate results; locate and fix problem and then rerun demonstration for those analytes that did not meet criteria.
Method blank.	One per analytical batch.	No analytes detected >MQL.	Correct problem then re-prep and analyze method blank and all samples.
LCS (1016/1260 mix).	One LCS per analytical batch.	QC acceptance criteria, Table 20.2.	Correct problem. Re-prep & analyze all associated samples.
Surrogate spike.	All samples	QC acceptance criteria, Table 20.2 & 20.3.	Method 8000, Section 8.6 Requirements. Describe in Checklist.
MS/MSD (1016/1260 mix).	One MS/MSD per every 20 project samples per matrix.	QC acceptance criteria, Table 20.3.	Describe in Laboratory Review Checklist.
MDL study.	Once per 12 month period.	Detection limits established shall be $\leq \frac{1}{2}$ the MQLs in table 21.1.	None.

APPENDIX C

EXAMPLE CHAIN-OF-CUSTODY FORM



Environmental Quality Management, Inc. Chain of Custody Record

COC Tracking: EQ- 20947

Project No.		Project Name				No. of Containers	TESTS																	
Samplers/Affiliation: (Print Name and Sign)				Lab P.O. No:																				
Sample ID:	Date	Time	Description/Matrix:	Sample Volume / Comments																				
Relinquished by: (Signature)	Date	Time	Received by: (Signature)		Date	Time	Ship To:																	
Relinquished by: (Signature)	Date	Time	Received by: (Signature)		Date	Time																		
Relinquished by: (Signature)	Date	Time	Received by: (Signature)		Date	Time	Airbill Number																	
Reporting/QA Requirements:	Turn Around Time (EXACT DUE DATE):			Report To:			Chain of Custody Seal Numbers																	

Distribution: White - Accompanies Shipment Pink - Project Files Yellow - Laboratory File