Gannett Fleming

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October 30, 2017
File #34283.000

Mr. Howard Caine – SR-6J
Remedial Project Manager
Waste Management Division
USEPA Region V
77 West Jackson Boulevard
Chicago, Illinois 60604-3590

Ms. Mae Willkom
Wisconsin Department of Natural Resources
1300 W. Clairemont Avenue
Eau Claire, Wisconsin 54702

Re: QAPP for Groundwater and SVE System Monitoring
National Presto Industries, Inc., Superfund Site, Eau Claire, Wisconsin
USEPA CERCLIS ID WID006196174
WDNR BRRTS 02-09-000267 and FID 609038320

Dear Howard and Mae:

At Howard's request, Gannett Fleming Inc. is submitting the referenced Quality Assurance Project Plan (QAPP) for groundwater and soil vapor extraction (SVE) monitoring at the National Presto Industries, Inc. (NPI) Superfund site in Eau Claire, Wisconsin. As described in the QAPP, the enclosed document is meant to supersede all QAPPs previously submitted for the NPI site and focus on current activities. If you have any questions during your review, please call.

Sincerely,

GANNETT FLEMING, INC.

Clifford C. Wright, P.E., P.G.
Project Engineer

Dennis Kugle
Sr. Project Manager

CCW/jec/Enc.

ecc: Alida Roberman (USEPA)
Mark Wichman (USACE)
Derrick Paul (NPI)

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Gannett Fleming

Excellence Delivered As Promised

Prepared for:

NATIONAL PRESTO INDUSTRIES, INC.
EAU CLAIRE, WISCONSIN

QUALITY ASSURANCE PROJECT PLAN
for
GROUNDWATER AND SOIL VAPOR EXTRACTION SYSTEM MONITORING

PROJECT #34283.000
OCTOBER 2017

Office Location:
GANNETT FLEMING, INC.
8025 Excelsior Drive
Madison, Wisconsin 53717-1900

Office Contacts:
Dennis Kugle
Cliff Wright, P.E., P.G.
608-836-1500

CONTENTS

FIGURES

TABLES

APPENDICES

ACRONYMS AND ABBREVIATIONS

AOC	Administrative Order on Consent
ARARs	Applicable or Relevant and Appropriate Requirements
AWS	Alternate Water Supply
BTU/lb	British thermal units per pound
Cd	Cadmium
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	Chain of Custody
DOA	Department of the Army
DCE	Dichloroethene
ELCR	Excess lifetime cancer risk
ECMWF	Eau Claire Municipal Well Field
EDS	East Disposal Site
EPA	United States Environmental Protection Agency
ES	(Wisconsin Administrative Code Ch. NR140) Enforcement Standard
ESD	Explanation of Significant Differences
FS	Feasibility Study
GF	Gannett Fleming, Inc.
HI	Hazard Index
ICs	Institutional Controls
IRM	Interim Remedial Measure
MCL	Maximum Contaminant Level
MRDS	Melby Road Disposal Site
NDC	National Defense Corporation
NPI	National Presto Industries, Inc.
O&M	Operation and Maintenance
OSWER	Office of Solid Waste and Emergency Response
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
PAH	Polycyclic aromatic hydrocarbon
PAL	(Wisconsin Administrative Code Ch. NR140) Preventive Action Limit
PCE	Perchloroethylene or perchloroethene or tetrachloroethene
PM	Project Manager
RAOs	Remedial Action Objectives
RI	Remedial Investigation
ROD	Record of Decision
RPM	Remedial Project Manager
SDWA	Safe Drinking Water Act

SVE	Soil Vapor Extraction
SWC	Southwest Corner (of the site)
TCE	Trichloroethylene
TCA	Trichloroethane
UAO	Unilateral Administrative Order
UFP	Uniform Federal Policy
UU/UE	Unlimited Use or Unrestricted Exposure
VOC	Volatile Organic Compound
WAC	Wisconsin Administrative Code
WDNR	Wisconsin Department of Natural Resources

1.0 INTRODUCTION

This quality assurance project plan (QAPP) has been prepared to supersede all prior QAPPs prepared for the National Presto Industries, Inc. (NPI) site in Eau Claire, Wisconsin, and focus on current activities. Dissolved-phase volatile organic compounds of concern at the site are limited to trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), tetrachloroethylene (PCE), 1,1-dichloroethane (DCA), and 1,1,-dichloroethylene (DCE). For the purpose of this QAPP, they will hereafter be referred to as the NPI volatile organic compounds (NPI VOCs).

The remedial investigations and feasibility study (RI/FS) at the site were completed in the early 1990s. Most of the selected interim and final remedies for the site were implemented in the mid- to late 1990s. These included:

- The excavation and off-site disposal of waste forge compound.
- The installation of four groundwater extraction wells and two associated cascade aerators for groundwater capture, control, and treatment.
- The construction of an engineered landfill and soil vapor extraction (SVE) system at the Melby Road Disposal Site (MRDS) for the long-term management of residual waste forge compound and impacted soil.

Since then, two additional, relatively small TCE source areas have been identified in what is known as the Southwest Corner (SWC), the MW-34/70 Area, and an area beneath the main building. SVE systems have been installed and are currently operating at both of these areas to remove VOCs in the soil and provide a barrier to migration of these chemicals to groundwater.

All active remediation systems onsite are effective in protecting human health and the environment. Three of the four groundwater extraction wells (EW-1R, EW-2, and EW-5) and one of the cascade aerators (CAS-1) are no longer in use as a result of the effectiveness of the remedial actions that have been implemented. Current and planned future activities at the site include:

- Maintenance of the cap at the MRDS.
- Operation and maintenance (O&M) of the three SVE systems and extraction well EW-6.
- Routine sampling of select on- and off-site groundwater monitoring wells/piezometers, EW-6, cascade aerator CAS-2R, manhole MH-18, city water supply wells and unit operations at the Eau Claire Municipal Well Field (ECMWF), and the exhaust gas from the MRDS, MW-34/70 area, and main building SVE systems.

- Supplemental soil sampling in the MW-34/70 area in August 2023. However, NPI will submit a work plan to the agencies for review prior to collecting the supplemental soil samples, as agreed. Consequently, worksheets for soil media are not included with this QAPP.

This QAPP describes:

- The procedures used for collecting groundwater samples from the monitoring wells/piezometers; pumped groundwater samples from EW-6, CAS-2R, and MH-18 and at the ECMWF; and air/exhaust gas samples from the SVE systems.
- The QA/QC protocols followed for each.
- The reporting of the monitoring and sampling results to the U.S. Environmental Protection Agency (EPA) and Wisconsin Department of Natural Resources (WDNR).

Currently, the primary goals at the site are to monitor:

1. Groundwater quality to document its continued improvement.
2. The three SVE systems to optimize their efficiency and confirm that they are providing continued protection of the groundwater.

Section 2.0 of this QAPP includes a description of the site and its history, Section 3.0 describes the sampling design and rationale, and Section 4.0 provides the Uniform Federal Policy (UFP) QAPP worksheets.

2.0 SITE DESCRIPTION, HISTORY, CONTAMINATION AND REMEDIATION

2.1 Site Description

The NPI site is located at 3925 North Hastings Way in Eau Claire, Wisconsin. The 320-acre property lies within the City of Eau Claire, with the exception of a 9-acre parcel on the eastern part of the site that is located in the Village of Lake Hallie and a 4-acre parcel in the southern part of the property that is located in the Town of Seymour. Most of the NPI property is situated in Chippewa County, with a small portion located along the northern border of Eau Claire County. Figure 1 is an NPI site map. The Village of Lake Hallie is located north and east of the NPI property, while the City of Eau Claire is located south and west of the site.

The site is relatively flat and abuts a sandstone ridge to the south. The areas to the east, north, and west are also relatively level, generally sloping gradually toward the Chippewa River, which is located approximately 2 miles north and west of the site. Lake Hallie, an impounded remnant of a former channel of the Chippewa River, lies approximately 1 mile north of the site.

Extending northward from the northwestern portion of the site to Lake Hallie and westerly from the site to the Chippewa River are buried pre-glacial valleys within which sand and gravel deposits serve as a primary drinking water aquifer in the Eau Claire area. Approximately 2 miles west of the NPI site, the ECMWF draws groundwater from more of these buried deposits and provides drinking water for the City of Eau Claire. The direction of groundwater flow is controlled by the sandstone bedrock valleys beneath the sand and gravel, which carry groundwater to the northwest towards Lake Hallie and to the west towards the Chippewa River and the ECMWF site. The depth to bedrock is at or near the surface at the sandstone ridge in the extreme south central portion of the site and dips to the north and west. The top of bedrock is at least 100 feet below the ground surface (bgs) at the north and west property boundaries.

2.2 Site History

Prior to its purchase by the U.S. Government (War Department) in 1942, what is now the NPI site was owned by nine individuals and was predominantly farmland with isolated areas of woodlands. From 1942 to 1945, the site was a government-owned, contractor-operated producer of ordnance chemicals and radar tubes. NPI purchased the property from the Federal Government in 1947. The company initially manufactured household appliances and outboard motors at the facility. Wastes generated by these operations consisted of metals, oils, grease, and spent solvents. Beginning in 1951, NPI also began production of artillery shell fuses and aircraft parts, under military contracts. By 1954, NPI had dedicated the site entirely to defense-related manufacturing, primarily the production of metal parts for 105-MM and 8-inch artillery shells,

under contract with the Department of the Army (DOA). Early waste-handling practices included the use of dry wells and seepage lagoons. Wastes were also discharged to a former sand and gravel pit. The major waste stream was spent forge compound, which was composed of mineral oil, graphite, and asphalt.

Between 1959 and 1965, NPI engaged in little to no active production at the site. The site was again activated in 1966, and multi-shift production continued until the mid-1970s. From 1966 to 1969, spent forge compound was landfilled onsite. Except for a six-month research and development contract in late 1983 and early 1984, production of the 8-inch shells ceased in 1971. Production of the 105-MM projectiles ceased in 1980. Between 1981 and 1992, National Defense Corporation (NDC), a wholly-owned subsidiary of NPI, entered into annual standby contracts with the DOA to maintain the site in a high state of readiness. After the contracts ended in 1992, much of the equipment was disassembled and sold to other companies.

Current land use for the surrounding area is single-family residential and some commercial and industrial enterprises to the north and west. It is anticipated that these land uses will continue into the foreseeable future.

Water supply in the area of the site is drawn from groundwater by the City of Eau Claire and Lake Hallie municipal water supply systems.

2.3 Site Contamination and the Conceptual Site Model

Early waste-handling practices related to the manufacturing activities on the NPI site included the use of dry wells and seepage lagoons. Manufacturing wastes were also discharged to a former sand and gravel pit. The major waste stream was waste forge compound. NPI discharged wastewater containing significant amounts of waste forge compound to Lagoon #1, a remnant of the former sand and gravel pit. From 1966 to 1969, waste forge compound was also landfilled at the MRDS.

In March 1981, routine groundwater sampling by the State of Wisconsin detected VOCs in the City of Eau Claire's municipal water supply. Contaminants of concern included VOCs such as trichloroethylene (TCE), dichloroethene (DCE), dichloroethane (DCA), and tetrachloroethene (PCE). In addition to monitoring the municipal production wells, the City began testing private residential wells located immediately northeast of the ECMWF. VOCs were detected in several of the residential wells at concentrations above state and federal drinking water standards.

Ultimately, the NPI site was identified as the primary source of this contamination. The conceptual site model (CSM) is that contaminants observed in the source areas on the NPI property migrated vertically through the unconsolidated soils to the groundwater and then

traveled within the aquifer following the buried valleys. These valleys, which trend westerly toward the Chippewa River and ECMWF (Plume 1/2) and northwesterly toward Lake Hallie (former Plumes 3/4 and 5), control the direction of groundwater flow in the unconsolidated deposits in the area. Figure 1 is a 24-inch x 36-inch area-wide map showing the approximate location of Plume 1/2 and the former locations of Plume 3/4 and Plume 5, as defined by select VOCs in 1993. The outlines of the current/former plumes define a groundwater flow divide that bisects the NPI site along a northwesterly line.

2.4 Site Remediation

Remedial actions were implemented at numerous locations to address waste management areas of concern at the site, including:

- Lagoon #1: Between October 1993 and September 1994, approximately 1,100,000 gallons of pumpable waste forge compound (>5,000 BTU/lb) were removed from former Lagoon #1, blended with spent solvents, and transported via rail cars to CERCLA-approved cement kilns for use as a supplemental fuel. Between November 1994 and December 1995, approximately 5,000 cubic yards of waste forge compound solids (>5,000 BTU/lb) were removed from the former lagoon, packaged, and transported to CERCLA-approved cement kilns and burned as supplemental fuel. Forge compound mixed with soil from Lagoon #1 with <5,000 BTU/lb was placed beneath the cap at the MRDS. An SVE system was then installed and operated at the base of the excavated lagoon from September 1997 to August 1998 to remove VOCs that remained in soil beneath the former lagoon.
- Drainage Ditch #3: Soil contaminated with waste forge compound was placed under the cap at the MRDS.
- East Extension of Lagoon #1: Most of the impacted material was placed under the cap at the MRDS. Some was disposed of at an off-site licensed landfill.
- Dry Wells #2 and #5: Contaminated soil was disposed of at an off-site licensed landfill.
- East Disposal Site: Contaminated waste was placed under the cap at the MRDS.
- Swale between Former Lagoons #3 and #4: Contaminated soil was disposed of at an off-site licensed landfill.
- Southwest Corner of Former Lagoon #2: Contaminated soil was disposed of at an off-site licensed landfill.
- Loading Dock Area: Contaminated soil was disposed of at an off-site licensed landfill.

In conjunction with these and additional source removal activities conducted elsewhere onsite, starting in March 1994, groundwater pumping was conducted from extraction wells EW-1/EW-1R and EW-2 located at the MRDS and EW-3/EW-5 and EW-4/EW-6 in the SWC of the site for

hydraulic control and to prevent the off-site migration of dissolved-phase VOCs. EW-1 was replaced by EW-1R in September 1995, and EW-3 was replaced by EW-5 in January 2004. On October 6, 2010, groundwater pumping for hydraulic control at the MRDS ceased but continued at the SWC. In September 2011, EW-4 was replaced by EW-6. Discharge monitoring points are periodically sampled to track contaminant concentrations and document performance of the extraction wells and cascade aerators. These points include the operating extraction wells and MH-18 to the storm sewer, which discharges the combined flow of pumped groundwater (treated by cascade aeration) to the Chippewa River. In addition, on-going remedial activities include:

- Maintenance of the engineered cap at the MRDS.
- Operation and maintenance (O&M) of the SVE system at the MRDS.
- O&M of two supplemental SVE systems (MW-34/70 Area and inside the main building) in the SWC. Both of these systems were installed to address relatively small TCE source areas identified since the initial remedial activities summarized above were completed.

Since all of the above remedial actions were implemented, concentrations of the VOCs of concern have generally been on a decreasing trend. For example, VOC concentrations in all wells monitored, both on and off site, have been at or below their respective MCLs since June 2015.

Cadmium is also a concern in one relatively small area in the SWC. As of June 2017, the most recent analytical results of groundwater samples detected Cd in samples from seven on-site monitoring wells. Only one well (MW-10A) contained Cd concentrations above its 5 micrograms per liter MCL.

3.0 SAMPLING DESIGN AND RATIONALE

Figure 1 shows the extensive network of wells and piezometers historically used to monitor groundwater elevations and quality related to the NPI site. Wells that have been abandoned are shaded. Table 1 is a summary of the construction information for all monitoring and extraction wells associated with the NPI site. This summary table also identifies with which plume/former plume each well is/was associated and provides the grid coordinates for each well shown on Figure 1.

Figure 2 shows the locations of the three existing SVE systems and includes the local monitoring well network, extraction wells, cascade aerators, and MH-18 for reference.

3.1 Groundwater and Pumped Groundwater Sampling Description and Schedule

The groundwater sampling schedule has evolved over time. Samples are collected quarterly, but not all wells are sampled each quarter. The new data are evaluated each quarter. Once a year in the Annual Report, the sampling schedule for the next year is proposed, based on the historical data from each well, as well as the location/purpose of each well. If the quarterly data indicate that more or less frequent sampling is warranted, NPI will notify the EPA and WDNR, propose a revised frequency, as appropriate, and implement it.

Table 2 provides the NPI groundwater and pumped groundwater sampling schedule for 2017 and 2018. The schedule for 2018 is basically the same as the one of 2017; however, it does not include the biennial wells that are only sampled in odd numbered years, and the manhole MH-18 analytes are slightly different in odd and even numbered years. In 2017, samples will be collected for:

- NPI VOC analysis at least once from a total of 87 monitoring wells/piezometers, the 4 on-site extraction wells, and 7 city production wells during the four routine quarterly sampling rounds. In addition to collecting samples from the above wells/piezometers and MH-18, samples will also be collected of the combined pumpage from the production wells in the City's north well field, both before and after the air strippers and following routine water treatment and chlorination by the City. The data from the ECMWF and within the treatment system will be used to evaluate the impact of blending the water from several production wells on the TCE concentration and the efficiency of the air strippers in removing TCE from the pumped water.
- Cd analysis at least once from a total of 11 monitoring wells/piezometers, the 2 on-site extraction wells in the SWC, and MH-18.

- Hardness (as $CaCO_3$); chromium, chromium+6, copper, lead, nickel, and zinc as total metals; polycyclic aromatic hydrocarbons (PAHs); and pentachlorophenol analysis from MH-18.

Ms. Mary Wehbe, MCW Scientific Solutions, Cedar Park, Texas, will validate the water data. QAPP Worksheet #36 in Section 4.0 below summarizes data validation procedures, etc.

3.2 Air Sampling Description and Schedule

The NPI site currently has three separate SVE systems in operation. The purpose of these systems is to remove VOCs from the subsurface and provide a vapor barrier to protect/improve groundwater quality. The largest SVE system is at the MRDS, where 12 vent wells are located within the capped landfill, which primarily contains waste forge compound from historic disposal operations there and the remedial excavations summarized in the Site Remediation section above. There are also 4 interior soil gas monitoring points in the landfill and 13 soil gas monitoring points outside the perimeter of the landfill. In the SWC, the MW-34/70 Area SVE system is used to address residual VOC contamination from TCE degreaser sludge that was buried there in the mid-1900s. This system currently includes 6 vent wells. The main building SVE system, which includes just one vent well, is being used to address VOC impacts from a source area beneath the main building at NPI. The exact location of this source area is not known.

Exhaust gas samples are collected quarterly from the MRDS and main building SVE systems. The samples are analyzed for TCE, 1,1,1-TCA, PCE, and 1,1-DCA. The interior and perimeter soil gas monitoring points at the MRDS were originally used for field screening, but in 2000 and 2001, the EPA approved discontinuing screening these soil gas monitoring points, respectively, because of the consistently low or non-detectable VOC concentrations. The MW-34/70 Area SVE system is sampled annually and only for TCE. The exhaust gas samples are collected in Summa canisters supplied by the laboratory and analyzed using Method TO-15.

4.0 QAPP WORKSHEETS

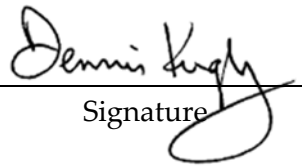
UFP-QAPP worksheets for the project follow. GF elected to use the March 2012 optimized UFP-QAPP worksheets, as discussed over the phone on June 7, 2017, with Howard Caine, the EPA Work Assignment Manager for the NPI site.

QAPP Worksheet #1 & 2: Title and Approval Page
(UFP-QAPP Manual Section 2.1)
(EPA 2106-G-05 Section 2.2.1)

Site name: National Presto Industries, Inc. (NPI)
Site location: Eau Claire, WI
EPA CERCLIS ID: WID 006196174
WDNR BRRTS: 02-09-000267 and FID: 609038320

Lead Consultant for NPI: Gannett Fleming, Inc. (GF)

GF Project Manager: Dennis Kugle



10/20/2017

Signature Date

GF Quality Manager: Cliff Wright

10/20/2017

Signature Date

Federal Regulatory Agency: United States Environmental Protection Agency (EPA)

EPA Work Assignment Manager: Howard Caine

Signature Date

Dates and Titles of QAPP Documents for Previous Work at NPI

- November 1987 – Quality Assurance Project Plan for Remedial Investigation/Feasibility Study.
- December 1993 – Revised Quality Assurance Project Plan for Interim Remedial Action Work Plan.
- April 1998 – Quality Assurance Project Plan for the Remedial Design/Remedial Action.

QAPP Worksheet #3 & 5: Project Organization and QAPP Distribution
(UFP-QAPP Manual Sections 2.3 and 2.4)
(EPA 2106-G-05 Sections 2.2.3 and 2.2.4)

A project organization chart follows. An asterisk is used to designate each QAPP recipient, as shown. Contact information for QAPP recipients is included on the following page.

EPA Region 5	EPA Region 5	WDNR
QAPP Reviewer	**Work Assignment Manager**	**Project Manager**
Alida Roberman*	Howard Caine*	Mae Willkom*

Gannett Fleming, Inc.
Project Manager
Dennis Kugle*
Quality Manager and Project Engineer
Cliff Wright*
Field Team
Chelsea Payne*
Marcus Mussey*

Analytical Laboratory
Pace Analytical Services, LLC
Dan Milewsky*-Green Bay, WI
Sarah Platzer*-Minneapolis, MN

Data Validator
MCW Scientific Solutions
Mary Wehbe*

*QAPP recipient.

QAPP Worksheet #3 & 5: Project Organization and QAPP Distribution (cont'd)
(UFP-QAPP Manual Sections 2.3 and 2.4)
(EPA 2106-G-05 Sections 2.2.3 and 2.2.4)

The QAPP distribution list follows.

Name	Title	Organization	Phone Number	Email Address
Howard Caine	Work Assignment Manager	EPA Region 5	312/353-9685	caine.howard@epa.gov
Alida Roberman	QAPP Reviewer	EPA Region 5	312/886-7336	roberman.alida@epa.gov
Mae Willkom	Project Manager (1)	WDNR	715/839-3748	mae.willkom@wisconsin.gov
	Regional mailbox (1)	WDNR		DNRRRWCR@wisconsin.gov
Derrick Paul	Project Manager	NPI	715/839-2141	dpaul@gopresto.com
Dennis Kugle	Project Manager	GF	608/836-1500 ext. 6705	dkugle@gfnet.com
Marcus Mussey	Project Geologist	GF	608/836-1500 ext. 6721	mmussey@gfnet.com
Chelsea Payne	Project Geologist	GF	608/836-1500 ext. 6718	cpayne@gfnet.com
Cliff Wright	Quality Manager and Project Engineer	GF	608/836-1500 ext. 6722	cwright@gfnet.com
Mary Wehbe	Contractor – Data Validation	MCW Scientific Solutions	512/970-4608	mary@mcwscientificsolutions.com
Sarah Platzer	Contractor – Air and Drinking Water Laboratory	Pace Analytical Services, LLC (Minneapolis, MN)	612/607-6451	Sarah.Platzer@pacelabs.com
Dan Milewsky	Contractor – Groundwater Laboratory	Pace Analytical Services, LLC (Green Bay, WI)	920/412-8566	dan.milewsky@pacelabs.com

FOOTNOTE:
(1) Email submittals to WDNR Project Manager and Regional mailbox and ship one paper copy to Project Manager per WDNR April 2017 guidance document RR-690.

QAPP Worksheet #4, 7, & 8: Personnel Qualifications and Sign-Off Sheet [1]
(UFP-QAPP Sections 2.3.2 – 2.3.4)
(EPA 2106-G-05 Sections 2.2.1 and 2.2.7)

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date
Organization: GF				
Dennis Kugle	Project Manager	BS Water Science, 41 years of experience		10/20/2017
Marcus Mussey	Project Geologist	BS Geology, 2 years of experience	40-hr OSHA HAZWOPER & current 8-hr update [2]	
Chelsea Payne	Project Geologist	BS Geology, 3 years of experience	40-hr OSHA HAZWOPER & current 8-hr update [2]	
Cliff Wright	Quality Manager and Project Engineer	BA Geology, MS Civil & Environmental Engineering, 35 years of experience	40-hr OSHA HAZWOPER & current 8-hr update, PE, PG	
Organization: MCW Scientific Solutions				
Mary Wehbe	Data Validator	BS Chemistry, 25 years of experience		
Organization: Pace Analytical Services, LLC [3]				
Dan Milewsky	Project Manager	BA Natural Resources, 21 years of experience		

FOOTNOTES:
(1) Signatures indicate that personnel have read and agree to implement this QAPP as written.
(2) GF field personnel have completed Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations and Emergency Response (HAZWOPER) 40-hour training, are current with the 8-hour annual refresher under 29 CFR 1910.120, and are trained in field procedures associated to assigned tasks. Additionally, all GF field personnel are trained in first aid/CPR.
(3) Dan Milewsky signs on behalf of Pace Analytical Services, LLC (Pace), including Sarah Platzer in Minneapolis, MN.

QAPP Worksheet #4, 7, & 8: Personnel Qualifications and Sign-Off Sheet [1]

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Gannett Fleming

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(UFP-QAPP Sections 2.3.2 – 2.3.4)
(EPA 2106-G-05 Sections 2.2.1 and 2.2.7)

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Cliff Wright	Quality Manager and Project Engineer	BA Geology, MS Civil & Environmental Engineering, 35 years of experience	40-hr OSHA HAZWOPER & current 8-hr update, PE, PG	CW / 10.20.17
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Marcus Mussey	Project Geologist	BS Geology, 2 years of experience	40-hr OSHA HAZWOPER & current 8-hr update [2]	
Chelsea Payne	Project Geologist	BS Geology, 3 years of experience	40-hr OSHA HAZWOPER & current 8-hr update [2]	
Cliff Wright	Quality Manager and Project Engineer	BA Geology, MS Civil & Environmental Engineering, 35 years of experience	40-hr OSHA HAZWOPER & current 8-hr update, PE, PG	
Organization: MCW Scientific Solutions				
Mary Wehbe	Data Validator	BS Chemistry, 25 years of experience		Mary C. Wehbe 10/20/17
Organization: Pace Analytical Services, LLC [3]				
Dan Milewsky	Project Manager	BA Natural Resources, 21 years of experience		

FOOTNOTES:

(1) Signatures indicate that personnel have read and agree to implement this QAPP as written.

(2) GF field personnel have completed Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations and Emergency Response (HAZWOPER) 40-hour training, are current with the 8-hour annual refresher under 29 CFR 1910.120, and are trained in field procedures associated to assigned tasks. Additionally, all GF field personnel are trained in first aid/CPR.

(3) Dan Milewsky signs on behalf of Pace Analytical Services, LLC (Pace), including Sarah Platzer in Minneapolis, MN.

QAPP Worksheet #4, 7, & 8: Personnel Qualifications and Sign-Off Sheet [1]

(UFP-QAPP Sections 2.3.2 – 2.3.4)

(EPA 2106-G-05 Sections 2.2.1 and 2.2.7)

Name	Project Title/Role	Education/Experience	Specialized Training/Certifications	Signature/Date
Organization: GF				
Dennis Kugle	Project Manager	BS Water Science, 41 years of experience		
Marcus Mussey	Project Geologist	BS Geology, 2 years of experience	40-hr OSHA HAZWOPER & current 8-hr update [2]	
Chelsea Payne	Project Geologist	BS Geology, 3 years of experience	40-hr OSHA HAZWOPER & current 8-hr update [2]	
Cliff Wright	Quality Manager and Project Engineer	BA Geology, MS Civil & Environmental Engineering, 35 years of experience	40-hr OSHA HAZWOPER & current 8-hr update, PE, PG	
Organization: MCW Scientific Solutions				
Mary Wehbe	Data Validator	BS Chemistry, 25 years of experience		
Organization: Pace Analytical Services, LLC [3]				
Dan Milewsky	Project Manager	BA Natural Resources, 21 years of experience		Dan Milewsky 10/19/17

FOOTNOTES:

(1) Signatures indicate that personnel have read and agree to implement this QAPP as written.

(2) GF field personnel have completed Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations and Emergency Response (HAZWOPER) 40-hour training, are current with the 8-hour annual refresher under 29 CFR 1910.120, and are trained in field procedures associated to assigned tasks. Additionally, all GF field personnel are trained in first aid/CPR.

(3) Dan Milewsky signs on behalf of Pace Analytical Services, LLC (Pace), including Sarah Platzer in Minneapolis, MN.

QAPP Worksheet #6: Communication Pathways

(UFP-QAPP Manual Section 2.4.2)

(EPA 2106-G-05 Section 2.2.4)

Communication Driver	Organization	Name [1]	Procedure (Timing, pathway, documentation, etc.)
Data validation issues [2]	MCW Scientific Solutions	Mary Wehbe	Contractor should contact GF Quality Manager by phone and email about any issue of note ASAP.
Laboratory issues-Green Bay [3]	Pace Analytical Services, LLC	Dan Milewsky	Contractor should contact GF Quality Manager by phone and email about any issue of note ASAP.
Laboratory issues-Minneapolis [3]	Pace Analytical Services, LLC	Sarah Platzer	Contractor should contact GF Quality Manager by phone and email about any issue of note ASAP.
Monthly and annual progress reports [4]	GF	Cliff Wright	Monthly progress reports on the O&M of the on-site groundwater extraction wells and Melby Road Disposal Site (MRDS) soil vapor extraction (SVE) system are submitted by email and paper copy (two of each report) delivery service to the EPA. In addition, annual status reports are submitted by email to the EPA and WDNR and paper copy to the WDNR.
Quarterly and annual DMRs	GF	Cliff Wright	Quarterly and annual discharge monitoring reports (DMRs) are submitted by email to the EPA and WDNR and a paper copy to the WDNR.
QAPP revisions	GF	Cliff Wright	QAPP changes during project execution will be as needed with EPA approval.
Regulatory agency interface	EPA	Howard Caine	Howard will contact Cliff Wright at GF by phone and email, as needed. In addition, EPA, WDNR, NPI, and GF representatives meet at the site to review progress annually.
Stop work authority [5]	GF	Chelsea Payne, Marcus Mussey	All field staff have the authority to stop work for health, safety, and/or QC concerns. In addition, field staff should communicate with the Quality Manager daily.

FOOTNOTES:

(1) See Worksheet #3 for phone number and email address contact information.

(2) Data validation issues include, but are not limited to, non-compliance with procedures and recommended data review corrective actions.

(3) Laboratory issues include, but are not limited to, sample receipt and lab QC variances and analytical corrective actions.

(4) Monthly progress reports are to be submitted in accordance with the requirements of the Administrative Order for Remedial Action between NPI and the EPA effective July 16, 1992, and the Unilateral Order between NPI, the EPA, and National Defense Corporation, effective October 21, 1993.

(5) Stop work due to health, safety, and/or quality control issues.

QAPP Worksheet #9: Project Planning Session Summary
(UFP-QAPP Manual Section 2.5.1 and Figures 9-12)
(EPA 2106-G-05 Section 2.2.5)

Not applicable because the project started in the 1980s, is ongoing, and no project planning sessions will be held for this QAPP.

QAPP Worksheet #10: Conceptual Site Model
(UFP-QAPP Manual Section 2.5.2)
(EPA 2106-G-05 Section 2.2.5)

See Section 2 for a description of the project's conceptual site model.

QAPP Worksheet #11: Project/Data Quality Objectives
(UFP-QAPP Manual Section 2.6.1)
(EPA 2106-G-05 Section 2.2.6)

This QAPP is an updated document for on-going work being conducted at NPI and describes the:

- Procedures used for collecting groundwater samples from existing monitoring wells; pumped groundwater samples from extraction well EW-6, cascade aerator CAS-2R, and manhole MH-18 and at the Eau Claire municipal well field (ECMWF); and exhaust gas samples from the SVE systems.
- QA/QC protocols followed for each sample type.
- Reporting of the monitoring and sampling results to the EPA and WDNR.

EPA Region 5, WDNR, and GF will use the data to document the quality of groundwater at and downgradient of NPI, support the shutdown of the groundwater extraction wells and cascade aerators used as interim remedial measures onsite and abandonment of monitoring wells, provide results for quarterly and annual discharge monitoring reports to the WDNR as needed, track NPI VOC levels at the ECMWF, monitor the performance of the three SVE systems, and ultimately provide a basis for delisting of the site.

Type of Data Needed

For groundwater samples collected from select wells, the target analyte list (TAL) VOCs of concern are trichloroethylene (TCE); 1,1,1-trichloroethane (TCA); tetrachloroethylene (PCE); 1,1-dichloroethane (DCA); and 1,1-dichloroethylene (DCE) and the TAL metal is dissolved cadmium (Cd).

For pumped groundwater samples collected at EW-6, CAS-2R, and the ECMWF the TAL VOCs of concern are TCE; 1,1,1-TCA; PCE; 1,1-DCA; and 1,1-DCE (i.e., the NPI VOCs).

For pumped groundwater samples collected at manhole MH-18, the TAL:

- Volatile organic compounds of concern are the NPI VOCs.
- Total metals are Cd, chromium, hexavalent chromium, copper, lead, nickel, and zinc.
- Also includes hardness (as $CaCO_3$), polycyclic aromatic hydrocarbons (PAHs), and pentachlorophenol. Parameters measured in the field include temperature and pH.

For the exhaust gas samples, the TAL VOCs are TCE; 1,1,1-TCA; PCE; and 1,1-DCA at the MRDS and main building SVE systems and TCE at the MW-34/70 area SVE system. The SVE exhaust gas at all three locations is also field screened for VOCs and methane using a hand-held flame-ionization detector (FID).

Data Quality Requirements to Support Environmental Decisions

The data need to be good enough to allow decisions to be made for groundwater sampling frequencies, number of wells to be sampled, the acceptability of abandonment of groundwater

monitoring wells/sampling points, shutdowns of groundwater extraction wells/cascade aerators, and operational changes to the SVE systems. Ultimately, the data will be used to support delisting of the site.

Data Collection and Generation

GF field staff, with help from NPI, will collect the samples. Pace Analytical Services, LLC (Pace or Pace Analytical) will generate the laboratory data. Groundwater samples will be analyzed by Pace's Green Bay, Wisconsin lab (Wisconsin Certification #405132750), and drinking water sample analysis will be performed by Pace's Minneapolis, Minnesota lab (Wisconsin Certification #999407970). Exhaust gas samples from the SVE systems will be analyzed by Pace Minneapolis (NELAP #1246636).

Data Reporting and Storage

Routine data will be submitted to the agencies in an annual report. Data specific to a trial shutdown, non-routine sampling, or special situation will be reported as agreed to on a case-by-case basis with the EPA.

Electronic copies of the analytical data are stored in the electronic project file. Field data are kept in the project notebook in GF's Madison, Wisconsin, office or on field data sheets, which are scanned and filed in the electronic project file.

QAPP Worksheet #12: Measurement Performance Criteria

(UFP-QAPP Manual Section 2.6.2)

(EPA 2106-G-05 Section 2.2.6)

Matrix	Water
Analytical Group	All

Analytical Method(s)	Data Quality Indicators (DQIs)	QC Sample or Measurement Performance Activity	Measurement Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
8260	Overall precision	Field Duplicates	≤ 50% RPD	S
2340B, 3500-Cr B, 6010, 8260, 8270	Completeness	See Worksheet #34	See Worksheet #34	S&A
2340B, 3500-Cr B, 6010, 8260, 8270	Accuracy / Bias	LCS/LCSD	See Worksheet #15	A
8260	Accuracy / Bias	MS/MSD	See Worksheet #15	S&A
8260	Precision	MS/MSD	See Worksheet #15	A

NOTES:
LCS/LCSD = Laboratory control sample/laboratory control sample duplicate.
MS/MSD = Matrix spike/matrix spike duplicate.
RPD = Relative percent difference.

QAPP Worksheet #12: Measurement Performance Criteria (cont'd)

(UFP-QAPP Manual Section 2.6.2)

(EPA 2106-G-05 Section 2.2.6)

Matrix	Air
Analytical Group	Select VOCs [1]

Analytical Method(s)	Data Quality Indicators (DQIs)	QC Sample or Measurement Performance Activity	Measurement Performance Criteria	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
TO-15	Completeness	See Worksheet #34	See Worksheet #34	S&A
TO-15	Accuracy / Bias	LCS/LCSD	See Worksheet #15	A
TO-15	Accuracy / Bias	MS/MSD	See Worksheet #15	A
TO-15	Precision	MS/MSD	See Worksheet #15	A

NOTES:
LCS/LCSD = Laboratory control sample/laboratory control sample duplicate.
MS/MSD = Matrix spike/matrix spike duplicate.

FOOTNOTE:
(1) For exhaust gas samples, the TAL VOCs are TCE; 1,1,1-TCA; PCE; and 1,1-DCA at the MRDS and main building SVE systems and TCE at the MW-34/70 area SVE system.

QAPP Worksheet #13: Secondary Data Uses and Limitations

(UFP-QAPP Manual Section 2.7)

(EPA 2106-G-05 Chapter 3: QAPP Elements for Evaluating Existing Data)

Data Type	Source	Data Uses Relative to Current Project	Factors Affecting the Reliability of Data and Limitations on Data Use
Historical lab data	Project files	Historical air analytical results will be used to show the correlation between relatively low vapor-phase TCA/TCE concentrations under the cap at the MRDS and improved groundwater quality there and estimate TCE mass removal by the MW-34/70 area and main building SVE systems. The historical groundwater and soil analytical results will be used to document groundwater trends and subsurface conditions, respectively, in future reports.	No known limitations, except as identified in lab reports and described in summary tables.

QAPP Worksheet #14/16: Project Tasks and Schedule [1]

(UFP-QAPP Manual Section 2.8.2)
(EPA 2106-G-05 Section 2.2.4)

Activity	Responsible Party	Planned		Deliverable(s)	Deliverable Due Date
		Start Date	Completion Date		
Monthly report	GF	Upon receipt of operating data from NPI	8/14/17	Monthly report for July 2017	8/31/17
Q3 monitoring	GF	9/5/17	9/7/17	2017 annual report	June 2018
Monthly report	GF	Upon receipt of operating data from NPI	9/15/17	Monthly report for Aug. '17	9/30/17
Annual report	GF	Started to compile data for report in 2016	10/2/17	2016 annual report	October 2017

FOOTNOTE:
(1) Current on-going activities at the site include O&M of EW-6 and the three SVE systems, quarterly monitoring, and monthly and annual reporting. This worksheet summarizes project tasks through September 2017.

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

(UFP-QAPP Manual Section 2.6.2.3 and Figure 15)

(EPA 2106-G-05 Section 2.2.6)

	NPI VOCs, select metals, hardness, PAHs, and pentachlorophenol - Water						
	Project Action Limit (PAL)		Project Action Limit Reference	Laboratory Specific [3]		Precision and Accuracy Method Performance Criteria [3]	
Analyte	Conc. [1] (µg/L)	Avg. [2] (lb/day)		LOQ (µg/L)	LOD (µg/L)	LCS/MS/MSD Recovery Limits (%)	LCS/MS/MSD Precision (RPD ≤)
Groundwater from wells/piezometers & pumped groundwater at ECMWF [4] & from EW-6 & MH-18 (within 60 feet of CAS-2R)[5]							
1,1-Dichloroethane	850	--	ES	1.0	0.24	70-133	20
1,1-Dichloroethene	7	--	MCL	1.0	0.41	70-130	20
Tetrachloroethylene	5	--	MCL	1.0	0.50	70-138	20
1,1,1-Trichloroethane	200	--	MCL	1.0	0.50	70-131	20
Trichloroethylene	5	--	MCL	1.0	0.33	70-130	20
Dissolved cadmium	5	--	MCL	5.0	1.3	75-125	20
Manhole MH-18 pumped groundwater discharge to the Chippewa River (via >2 miles of storm sewer)							
Cadmium, total recoverable	240	0.22	DL	5.0	1.3	75-125	20
Chromium	19,000	10	DL	5.0	1.5	75-125	20
Hexavalent chromium	240	--	DL	20	3.9	90-110	20
Copper	160	--	DL	10.0	3.4	75-125	20
Lead	1,300	1.3	DL	7.5	1.6	75-125	20
Nickel	11,000	13	DL	10.0	2.6	75-125	20
Zinc	1,000	--	DL	40.0	9.3	75-125	20
Hardness (as $CaCO_3$)	--	--	--	2,000	150	--	20
PAHs, total (summation)[6]	--	0.91	DL	--	--	--	--
Acenaphthene (PAH)	--	--	--	4.3	1.3	69-130	20
Acenaphthylene (PAH)	--	--	--	3.4	1.0	70-130	20
Anthracene (PAH)	--	--	--	5.7	1.7	70-130	20
Benzo(a)anthracene (PAH)	--	--	--	1.7	0.51	70-130	20
Benzo(a)pyrene (PAH)	--	--	--	6.0	1.8	61-130	20
Benzo(b)fluoranthene (PAH)	--	--	--	2.1	0.62	60-130	24
Benzo(g,h,i) perylene (PAH)	--	--	--	2.6	0.77	45-131	20
Benzo(k)fluoranthene (PAH)	--	--	--	3.2	0.95	55-142	20
Chrysene (PAH)	--	--	--	5.5	1.7	70-130	20

Analyte	NPI VOCs, select metals, hardness, PAHs, and pentachlorophenol - Water						
	Project Action Limit (PAL)		Project Action Limit Reference	Laboratory Specific (3)		Precision and Accuracy Method Performance Criteria (3)	
	Conc. (1) (µg/L)	Avg. (2) (lb/day)		LOQ (µg/L)	LOD (µg/L)	LCS/MS/MSD Recovery Limits (%)	LCS/MS/MSD Precision (RPD ≤)
Dibenzo(a,h)anthracene (PAH)	--	--	--	4.2	1.3	10-130	27
Fluoranthene (PAH)	--	--	--	1.8	0.54	65-130	20
Fluorene (PAH)	--	--	--	2.4	0.71	69-130	20
Indeno(1,2,3,c,d) pyrene (PAH)	--	--	--	4.8	1.4	34-133	25
1-Methylnaphthalene (PAH)	--	--	--	5.3	1.6	66-130	20
2-Methylnaphthalene (PAH)	--	--	--	4.8	1.7	68-130	20
Naphthalene (PAH)	--	--	--	6.0	1.8	70-130	20
Phenanthrene (PAH)	--	--	--	5.8	1.7	70-130	20
Pyrene (PAH)	--	--	--	4.3	1.3	64-130	20
Pentachlorophenol	70	--	DL	4.6	1.4	38-180	25

NOTES:

DL = Discharge limit in micrograms per liter (µg/L) or pounds per day (lb/day).
ES = NR 140 enforcement standard.
LCS/MS/MSD = Laboratory control sample/matrix spike/matrix spike duplicate.
LOD = Limit of detection.
LOQ = Limit of quantification.
MCL = Maximum contaminant level.
-- = Not applicable
PAHs = Polycyclic aromatic hydrocarbons.
RPD = Relative percent difference.
Aqueous samples may be diluted due to the presence of high levels of target and non-target analytes, or other matrix interferences.

FOOTNOTES:

(1) PAL Conc. = Threshold groundwater concentration for MCL/ES; DL for MH-18 pumped groundwater discharge to the river.
(2) PAL Avg. = Average mass DL for MH-18 pumped groundwater. Monthly average for PAHs; weekly average for other analytes.
(3) Laboratory LOD, LOQ, and Control Limits are subject to change.
(4) ECMWF samples analyzed for the NPI VOCs only.
(5) PAL MCL/ES thresholds apply to groundwater and ECMWF samples only, not to EW-6 and MH-18 pumped groundwater.
(6) PAHs, total = Summation of the 18 PAH compound concentrations shown, using LOD if not detected at or above a LOD.

QAPP Worksheet #15: Project Action Limits and Laboratory-Specific Detection/Quantitation Limits (cont'd)
(UFP-QAPP Manual Section 2.6.2.3 and Figure 15)
(EPA 2106-G-05 Section 2.2.6)

	Select VOCs – Air						
	Project Action Limit (PAL)			Laboratory Specific		Precision and Accuracy Method Performance Criteria	
Analyte	Conc. (µg/m³)	Emission Threshold [1]/Limit [2]	Project Action Limit Reference [3]	LOQ (µg/m³)	LOD (µg/m³)	LCS/MS/MSD Recovery Limits (%)	LCS/MS/MSD Precision (RPD ≤)
1,1-Dichloroethane	--	21.7 lb/day	Table A of NR 445.07	1.1	0.21	70-130	25
Tetrachloroethylene	--	9.11 lb/day	Table A of NR 445.07	0.92	0.37	70-130	25
1,1,1-Trichloroethane	--	--	--	1.5	0.33	70-134	25
Trichloroethylene	--	888 lb/yr	Table A of NR 445.07	0.74	0.37	70-130	25
Total VOCs [5]	--	5.7 lb/hr	NR 406.04(2)	--	--	--	--

NOTES:
Concentrations (Conc., LOQ, and LOD) are in micrograms per cubic meter (µg/m³).
Emission thresholds and limit are in pounds per hour (lb/hr), day (lb/day), or year (lb/yr), as shown.
LCS/MS/MSD = Laboratory control sample/ matrix spike/matrix spike duplicate.
LOD = Limit of detection.
LOQ = Limit of quantification.
RPD = Relative percent difference.
-- = Not applicable.

FOOTNOTES:
(1) Compound-specific emission thresholds, as defined in Table A of NR 445.07, when stack heights are less than 25 feet.
(2) Total VOC emission limit of 5.7 lb/hr is defined in NR 406.04(2), Wisconsin Administrative Code (Wis. Adm. Code).
(3) PAL references are to Sections NR 406.04(2) and NR 445.07, Wis. Adm. Code.
(4) The emission threshold for 1,1,1-TCA is not regulated by NR 445, Wis. Adm. Code.
(5) Total VOCs = summation of the detected concentrations of the four analytes shown.

QAPP Worksheet #17: Sampling Design and Rationale
(UFP-QAPP Manual Section 3.1.1)
(EPA 2106-G-05 Section 2.3.1)

See Section 3.0 for a description of the project's sampling design and rationale.

QAPP Worksheet #18: Sampling Locations and Methods

(UFP-QAPP Manual Section 3.1.1 and 3.1.2)
(EPA 2106-G-05 Section 2.3.1 and 2.3.2)

Sample ID	Matrix	Depth (ft bgs)	Type	Analyte/ Analytical Group	Sampling SOP	Comments
MW-X	Water	Screened interval (depth varies) or not applicable	Monitoring and extraction wells, piezometers, cascade aerators, MH-18, and the ECMWF	NPI VOCs and Cd, metals, PAHs, pentachlorophenol, and hardness	GF SOPs 1 and 2	X = Well number. An updated groundwater sampling schedule is submitted for review with each annual report and the Executive Summary to the QAPP worksheets.
SVE exhaust	Air	Not applicable	Summa canister grab sample	TCE; 1,1,1-TCA; PCE; and 1,1-DCA at the MRDS and main building SVE systems and TCE at the MW-34/70 area SVE system	GF SOPs 2 and 3	Field screen the vent wells and exhaust gas of each system for VOCs and methane using a portable FID quarterly, when operating. Sample the exhaust gas at the MRDS and main building SVE systems quarterly and the MW-34/70 area SVE system annually.

NOTES:
Maps showing the locations of the monitoring wells, piezometers, and SVE systems are provided with this report.
SOP = Standard operating procedure (see Appendix A for Pace SOPs and Appendix B for GF SOPs).

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

(UFP-QAPP Manual Section 3.1.2.2)
(EPA 2106-G-05 Section 2.3.2)

Analytical Group	Matrix	Method/ SOP [1]	Containers	Preservation	Holding Time [2]		Data Pack Turnaround
					Preparation	Analysis	
VOCs	Air	TO-15	One 1-L or 6-L Summa can	None	30 days	30 days	28 days
VOCs	Water	SW846/8260 and 524.2	3x40 mL glass VOA vial	No headspace, HCL to pH<2, ≤6°C	7 days	14 days	28 days
Metals (except Hex Cr)	Water	6010	250 mL plastic	HNO_3 to pH<2	6 months	6 months	28 days
Hexavalent chromium	Water	SM 3500Cr-B	250 mL plastic (glass ok)	None	24 hours	24 hours	28 days
Hardness	Water	SM 2340B	250 mL plastic	HNO_3 to pH<2	6 months	6 months	28 days
PAHs	Water	8270C SIM	100 mL amber glass, narrow mouth (NM)	None	7 days	7 days	28 days
PAH and/or Pentachlorophenol	Water	8270C	1 L amber glass, NM	None	7 days	7 days	28 days

NOTES:
HCL = Hydrochloric acid. HNO_3 = Nitric acid. PAH = Polycyclic aromatic hydrocarbons. VOCs = Volatile organic compounds.

FOOTNOTES:
(1) See Worksheet #23 and Pace SOPs in Appendix A.
(2) Laboratory reference information is summarized below. See Worksheet #3 for Pace point of contact email and phone numbers. No back-up laboratory is currently under contract; however, qualified alternative laboratories do exist.

Matrix	Laboratory		Delivery Method	Required Certification
	Sample Receipt Address	Point of Contact		
Air	Pace Analytical, 1700 Elm Street, Suite 200, Minneapolis, MN 55414	Sarah Platzer	Ground okay	NELAP # 1246636
Water	Pace Analytical, 1241 Bellevue Street, Suite 9, Green Bay, WI 54302	Dan Milewsky	Overnight courier	WI #405132750
Water	Pace Analytical, 1700 Elm Street, Suite 200, Minneapolis, MN 55414	Sarah Platzer	Overnight courier	WI #999407970

QAPP Worksheet #20: Field QC Summary [1]
(UFP-QAPP Manual Section 3.1.1 and 3.1.2)
(EPA 2106-G-05 Section 2.3.5)

Matrix	Analytical Group	Field Samples [2]	Field Duplicates	Matrix Spike (MS)	Matrix Spike Duplicate (MSD)	Field Blanks	Equipment Blanks	Trip Blanks	Total Number of Samples to Lab
Air [3]	Select VOCs	3	0	0	0	0	0	0	3
Water	NPI VOCs	34	4[4]	2[5]	2[5]	0	0	2[6]	44
Water	Cd	5	0	0	0	0	0	0	5

FOOTNOTES:
(1) Summary of the types of samples to be collected and analyzed for the third quarter (Q3) of 2017.
(2) Number of locations where samples for laboratory analysis will be collected.
(3) Q3 exhaust gas samples from the MRDS and main building SVE systems and annual sample from the MW-34/70 area SVE system.
(4) Collect 1 field duplicate for NPI VOCs per 10 sample locations.
(5) Collect 1 MS and 1 MSD for NPI VOCs per 20 sample locations.
(6) Include one trip blank for NPI VOCs in each cooler containing NPI VOC samples shipped to the lab.

QAPP Worksheet #21: Field SOPs
(UFP-QAPP Manual Section 3.1.2)
(EPA 2106-G-05 Section 2.3.2)

SOP No.	Title	Originating Organization	SOP Option or Equipment Type (1)	Modified for Project?	Comments
SOP-1	Groundwater Sampling and Equipment Decontamination	GF	PDBs and HydraSleeves®	No	See below (2)
SOP-2	Groundwater Sample Handling and QA/QC Protocols	GF	Not applicable	No	See below (2)
SOP-3	SVE Exhaust Gas Sampling	Pace	Not applicable	No	See below (3)
SOP-4	Well Abandonment	WDNR	Not applicable	No	See below (4)

FOOTNOTES:
(1) If the SOP provides different options, then the preferred alternative or equipment type is listed in this column.
(2) SOP by GF is included in Appendix B.
(3) SOP by Pace provides instructions for Summa canister grab sampling, and a copy is included in Appendix B.
(4) SOP for well abandonment is Section NR 141.25, Wisconsin Administrative Code, and a copy is included in Appendix B.

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

(UFP-QAPP Manual Section 3.1.2.4)
(EPA 2106-G-05 Section 2.3.6)

Field Equipment	Activity	SOP Reference	Title or Position of Responsible Person	Frequency	Acceptance Criteria	Corrective Action
Electric water level indicator	Clean (1) and inspect	Not applicable	Field staff	At the start of each day and between each well	Not applicable	Replace battery or replace meter
FID and water quality meter	Calibration	Not applicable	Qualified service technician	Annual	Meets manufacturer's specifications	Recalibrate, clean, or replace
Water quality meter	Calibration (2)	Not applicable	Field staff	At the start of each day	Readings match calibration standards	Recalibrate, clean, or replace

FOOTNOTES:
(1) The tape and probe will be cleaned with paper towels, a potable water/Alconox solution, and potable rinse water between each use. The paper towels will be properly disposed of after each use.
(2) Manufacturer's instructions and calibration supplies will accompany equipment into the field.

QAPP Worksheet #23: Analytical SOPs
(UFP-QAPP Manual Section 3.2.1)
(EPA 2106-G-05 Section 2.3.4)

Lab SOP [1]	Title, Date, and URL (if available)	Definitive or Screening Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project?
S-GB-I-045	Chromium, Hexavalent-Colorimetric	Definitive	Hexavalent Chromium	Spectrophotometer	No
S-GB-M-005	Determination of Metals by Inductively Coupled Plasma (ICP)_Spectroscopy (06/21/2017)	Definitive	Water/hardness	ICP	No
S-GB-O-049	Determination of Semi-Volatile Organics by GC/MS (06/21/2017)	Definitive	Water/Pentachlorophenol	GC/MS	No
S-GB-O-050	Determination of Semi-Volatile Organics by GC/MS and SIM (Selective Ion Monitoring) (10/24/2016)	Definitive	Water/PAHs	GC/MS	No
S-GB-O-056	Determination of Volatile Organics by GC/MS (06/21/2017)	Definitive	Water/NPI VOCs	GC/MS	No
S-MN-A-013	Analysis of Whole Air Samples for Volatile Organic Compounds by GC/MS (TO15)	Definitive	Air/NPI VOCs	GC/MS	No
S-MN-O-546	Analysis of Volatile Organic Compounds in Water (524.2)	Definitive	Water/DW VOCs	GC/MS	No

FOOTNOTE:
(1) See Pace SOPs in Appendix A.

QAPP Worksheet #24: Analytical Instrument Calibration [1]

(UFP-QAPP Manual Section 3.2.1)
(EPA 2106-G-05 Section 2.3.6)

Instrument	Calibration			Acceptance Criteria	Corrective Action (CA)	Responsible Person for CA	Lab SOP [2]
	Procedure	Range	Frequency				
GC/MS	Tuning, etc. [3]	See SOP	See SOP	See SOP	See SOP	Pace analyst	S-GB-O-049 S-GB-O-050 S-GB-O-056
ICP	Calibration, etc. [3]	See SOP	See SOP	See SOP	See SOP	Pace analyst	S-GB-M-005
Spectrophotometer	Calibration, etc. [3]	See SOP	See SOP	See SOP	See SOP	Pace analyst	S-GB-I-045
GC/MS	Tuning, Calibration, etc. [3]	See SOP	See SOP	See SOP	See SOP	Pace analyst	S-MN-A-013
GC/MS	Tuning, Calibration etc. [3]	See SOP	See SOP	See SOP	See SOP	Pace analyst	S-MN-O-546

FOOTNOTES:
(1) Also see Worksheet #15.
(2) See Pace SOPs in Appendix A.
(3) Procedures described in the SOP include tuning (if applicable), initial calibration, calibration blank, initial and continuing calibration verifications, and verification of detection and quantification limits, as applicable.

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

(UFP-QAPP Manual Section 3.2.3)

(EPA 2106-G-05 Section 2.3.6)

Not applicable because both Pace laboratories operate under quality systems that conform to ISO 17025:2005 and NELAC Institute and WDNR standards. The labs' current quality manuals are both revision number 19 dated April 27, 2017, for Pace Green Bay and June 19, 2017, for Pace Minneapolis.

QAPP Worksheet #26 & 27: Sample Handling, Custody, and Disposal
(UFP-QAPP Manual Section 3.3)
(EPA 2106-G-05 Section 2.3.3)

Sampling organization: GF
Laboratory: Pace Analytical Services, LLC (Pace)
Method of sample delivery: Overnight courier for water samples; ground is okay for air.
Number of days from reporting until sample disposal: 30 days for water; sample disposal occurs following analysis for air.

Activity	Organization and Title or Position of Person Responsible for Activity	SOP No. (1)
Sample labeling	GF project geologist/field staff	2
Chain-of-custody (COC) form completion	GF project geologist/field staff	2
Packaging	GF project geologist/field staff	2
Shipping coordination	GF project geologist/field staff	2
Sample receipt, inspection, and login	Pace sample receipt staff	2
Sample custody and storage	Pace sample custodian	2
Sample disposal	Pace lab staff	2

FOOTNOTE:
(1) GF SOP 2 in Appendix B includes descriptions of sample labeling; COC form completion; packaging; shipping coordination; sample receipt, inspection, and login; sample custody and storage; and sample disposal protocols.

Example blank COCs from Pace Green Bay and Pace Minneapolis are included in Appendix C.

QAPP Worksheet #28: Analytical Quality Control and Corrective Action
(UFP-QAPP Manual Section 3.4 and Tables 4, 5, and 6)
(EPA 2106-G-05 Section 2.3.5)

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action (CA)	Responsible Person for CA	Project-Specific MPC
Matrix: air, Analytical Group: select VOCs, Analytical Method: TO-15					
Method blank	1 per ≤20 samples	An instrument blank analysis is allowed after any sample that has known VOCs present that exceed the upper calibration limit of the method to demonstrate that the system is free of possible carryover effects. When possible, historical data can be used to determine if there are high levels of contaminants present, possibly causing carryover in the system. The method blank must not contain any target analyte at a concentration greater than its reporting limit and must not contain additional compounds with elution	Re-analyze associated samples. Exceptions: If sample ND, report sample without qualification. If sample result >10x MB detects, report the data since it is not impacted by the blank detections. If sample result <10x MB detects and cannot be re-prepared/ reanalyzed, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.	Pace project manager	

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action (CA)	Responsible Person for CA	Project-Specific MPC
		characteristics and mass spectral features that interfere with identification and measurement of a method analyte. The internal standard must be within ± 40% of the mean area response of the IS in the most recent calibration. The retention time of each of the internal standards must be within ± 0.33 minutes between the method blank and the most recent calibration standard.			
Lab Control Sample	1 per ≤20 samples	The percent recovery for each analyte in the LCS must be within the internally generated recovery limits and can be found in the LIMS system.	If a LCS fails to meet the recovery limit criteria, inspect the system for the possibility of a poor sampling. If the LCS fails and no error in sampling was found, preparation and injection of a second analysis can be conducted. If that	Pace project manager	

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action (CA)	Responsible Person for CA	Project-Specific MPC
			second analysis fails, the system must be recalibrated, and all affected samples must be reanalyzed. If the samples cannot be reanalyzed, qualify the data accordingly with an appropriate footnote on the final report indicating the bias present.		
Matrix: water, Analytical Group: NPI VOCs, Analytical Method: 8260					
Method blank	1 per ≤20 samples	No analyte > QL	Apply qualifier if concentration >MDL and <QL. If >QL, correct problem, then repeat prep and analysis of method blank and all samples with detects greater than the maximum of (1) the limit of detection; (2) five percent of the regulatory limit; or (3) ten percent of the measured concentration.	Pace project manager	
Lab Control Sample	1 per ≤20 samples	See Worksheet 15	Assess all other batch QC for same bias, if consistent bias present, repeat prep	Pace project manager	

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action (CA)	Responsible Person for CA	Project-Specific MPC
			and analysis of LCS and all samples in the affected analytical batch.		
Matrix: water, Analytical Group: metals, Analytical Method: 6010					
Method blank	1 per ≤20 samples	No analyte > QL	Apply qualifier if MB concentration >MDL and <QL and sample levels <10X MB. If >QL, correct problem, then repeat prep and analysis of method blank and all samples processed with the contaminated blank.	Pace project manager	
Lab Control Sample	1 per ≤20 samples	80-120%	Terminate analysis, correct problem, redigest and reanalyze all samples associated with the LCS.	Pace project manager	
Matrix: water, Analytical Group: hexavalent chromium, Analytical Method: 3500Cr-B					
Method blank	1 per ≤20 samples	No analyte > QL	Apply qualifier if MB concentration >MDL and <QL and sample levels <10X MB. If >QL, correct problem, then repeat prep and analysis of method blank and all samples processed with the contaminated blank.	Pace project manager	
Lab Control Sample	1 per ≤20 samples	90-110%	Terminate analysis, correct problem,	Pace project manager	

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action (CA)	Responsible Person for CA	Project-Specific MPC
			redigest and reanalyze all samples associated with the LCS.		
Matrix: water, Analytical Group: hardness, Analytical Method: 2340B					
Method blank	1 per ≤20 samples	No analyte > QL	Apply qualifier if MB concentration >MDL and <QL and sample levels <10X MB. If >QL, correct problem, then repeat prep and analysis of method blank and all samples processed with the contaminated blank.	Pace project manager	
Lab Control Sample	1 per ≤20 samples	80-120%	Terminate analysis, correct problem, redigest and reanalyze all samples associated with the LCS.	Pace project manager	
Matrix: water, Analytical Group: PAHs and pentachlorophenol, Analytical Method: 8270					
Method blank	1 per ≤20 samples	No analyte > QL	Apply qualifier if concentration >MDL and <QL. If >QL, correct problem, then repeat prep and analysis of method blank and all samples with detects greater than the maximum of (1) the limit of detection; (2) five percent of the regulatory limit; or (3) ten percent of the	Pace project manager	

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action (CA)	Responsible Person for CA	Project-Specific MPC
			measured concentration.		
Lab Control Sample	1 per ≤20 samples	See Worksheet 15	Assess all other batch QC for same bias; if consistent bias present, repeat prep and analysis of LCS and all samples in the affected analytical batch.	Pace project manager	
Matrix: water, Analytical Group: DW VOCs, Analytical Method: 524.2					
Method blank	1 per ≤20 samples	Target analytes must be less than one-half the reporting limit. If results are reported to MDL, target analytes in MB should be non-detect.	Re-analyze associated samples. Exceptions: If sample ND, report sample without qualification. If sample result >10x MB detects, report sample as not impacted by the blank contamination. If sample result <10x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier. Client must be alerted and authorize this condition.	Pace project manager	

QC Sample	Number/Frequency	Method/SOP Acceptance Criteria	Corrective Action (CA)	Responsible Person for CA	Project-Specific MPC
Lab Control Sample	1 per ≤20 samples	%Rec: 70-130% for all analytes %Diff ≤ 20%	Check spike solution and remake accordingly. Perform system maintenance determined necessary and reanalyze one time. Since this is the CCV, only two tries are allowed before recalibration is required. Exceptions: If LCS recovery is > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. Or if insufficient sample is available, notify the project manager and qualify the data accordingly.	Pace project manager	

QAPP Worksheet #29: Project Documents and Records
(UFP-QAPP Manual Section 3.5.1)
(EPA 2106-G-05 Section 2.2.8)

Record Type	Generation	Verification	Storage Location
Sample Collection and Field Records			
Field book/field data sheets	GF field staff	GF quality manager	Project file
Chain-of-custody (COCs) records	GF field staff	GF quality manager	Project file
QC reports	GF quality manager	GF project manager	Project file
Deviations	GF quality manager	GF project manager	Project file
Corrective action reports	GF quality manager	GF project manager	Project file
Correspondence	GF project engineer	GF project manager	Project file
Project Assessments			
Data validation report	Mary Wehbe	GF quality manager	Project file
Laboratory Records			
Sample receipt & COC records	Pace	Pace project manager	Project file
Instrument calibration logs	Pace	Pace project manager	Project file
Sample prep logs	Pace	Pace project manager	Project file
Equipment maintenance logs	Pace	Pace project manager	Project file
Corrective action reports	Pace	Pace project manager	Project file
QC results	Pace	Pace project manager	Project file

QAPP Worksheet #29: Project Documents and Records (cont'd)

(UFP-QAPP Manual Section 3.5.1)

(EPA 2106-G-05 Section 2.2.8)

Laboratory Data Deliverables				
Record	**VOCs**	**Metals (1)**	**SVOCs (2)**	**Hardness (as $CaCO_3$)**
Narrative	X	X	X	X
Summary results	X	X	X	X
QC results	X	X	X	X
COC	X	X	X	X

FOOTNOTES:

(1) Metals include hexavalent chromium.

(2) SVOCs include PAHs and pentachlorophenol.

QAPP Worksheet #31, 32, & 33: Assessments and Corrective Action
(UFP-QAPP Manual Section 4.1.1 and 4.1.2)
(EPA 2106-G-05 Section 2.4 and 2.5.5)

Assessment Response and Corrective Action [(1)]:

Assessment Type	Responsible for Responding to Assessment Findings	Assessment Response Documentation	Timeframe for Response	Corrective Action Responsibilities	
				Implementation	Monitoring of Implementation
Field sampling TSA	GF field team leader	Field Sampling CA Response	24 hours from receipt of memo	GF field team leader	GF quality manager
Proficiency testing (PT) samples	Lab QC manager	PT Deficiency Response	7 days following receipt of PT deficiency notice and before analysis of field samples	Lab technical director	Pace project manager

NOTES:
CA = Corrective Action
TSA = Technical systems audit

FOOTNOTE:
(1) No assessment audits prior to the start of sampling will be conducted because this is an on-going project.

QAPP Worksheet #34: Data Verification and Validation Inputs

(UFP-QAPP Manual Section 5.2.1 and Table 9)
(EPA 2106-G-05 Section 2.5.1)

Item	Description	Verification (Completeness)	Validation (Conformance to Specifications)
Planning Documents/Records			
1	Approved UFP-QAPP	X	
2	Field SOPs	X	
3	Laboratory SOPs	X	
Field Records			
4	Field books/field data sheets	X	
5	Equipment calibration records	X	
6	Chain-of-custody records	X	
7	Relevant correspondence	X	
Analytical Data Package			
8	Cover sheet (laboratory identifying information)	X	X
9	Case narrative	X	X
10	Internal laboratory chain-of-custody	X	X
11	Sample receipt records	X	X
12	Sample chronology (1)	X	X
13	LOD/LOQ establishment and verification	X	X
14	Standards traceability	X	X
15	Instrument calibration records	X	X
16	Definition of laboratory qualifiers	X	X
17	Results reporting forms	X	X
18	QC sample results	X	X
19	Corrective action reports	X	X

FOOTNOTE:
(1) Sample chronology includes dates and times of receipt, preparation, and analysis.

QAPP Worksheet #35: Data Verification Procedures
(UFP-QAPP Section 5.2.2)
(EPA 2106-G-05 Section 2.5.1)

Records Reviewed	Requirement Documents	Process Description	Responsible Person, Organization
Field book/field data sheets	QAPP, GF SOP 2 (Appendix B)	Field notes will be recorded daily to document sample locations, verify that all planned samples were collected, and describe any deviations from the plan.	Daily: Field staff, GF At conclusion of field activities: QM, GF
Chain-of-custody (COC) forms	QAPP, GF SOP 2 (Appendix B)	COC records will be reviewed for completeness and verified against the field data sheets and samples in the cooler. COCs will be signed and copies will be retained for the project file.	Daily: Field staff, GF At conclusion of field activities: QM, GF
Laboratory Deliverable	QAPP	Verify that the laboratory deliverable contains all records specified in the UFP-QAPP. Check sample receipt records to ensure that sample condition upon receipt was noted and any missing/broken sample containers were noted and reported according to plan. Compare the data package with the COCs to verify that results were provided for all collected samples. Review the narrative to ensure all QC exceptions were described. Check for evidence that any required notifications were provided to project personnel as specified in the UFP-QAPP. Verify that necessary signatures and dates are present.	Before release: Lab QAM, Pace Upon receipt: QM, GF
Audit Reports, Corrective Action Reports	QAPP	Verify that all planned audits were conducted. Examine audit reports. For any deficiencies noted, verify that corrective action was implemented according to plan.	Lab-specific: Lab QAM, Pace Project-related: QM, GF

NOTES:
QAM = Quality Assurance Manager.
QM = Quality Manager.

QAPP Worksheet #36: Data Validation Procedures
(UFP-QAPP Section 5.2.2)
(EPA 2106-G-05 Section 2.5.1)

Matrix:	**Air**	**Water**	**Water**	**Water**
Analytical Group/Method:	VOCs/TO-15	VOCs/8260 and 524.2	Metals/6010 and 3500Cr-B	SVOCs/8270
Data deliverable requirements:	PDF of data package	PDF of data package	PDF of data package	PDF of data package
Analytical specifications:	WS 28	WS 28	WS 28	WS 28
Measurement performance criteria:	WS 12	WS 12	WS 12	WS 12
% of data packages to be validated:	0	10	100	100
Validation procedure:	Not applicable	EPA (1)	EPA (2)	EPA (1)

FOOTNOTES:
(1) Guidance documents include "National Functional Guidelines for Superfund Organic Methods Data Review" dated September 2016 and January 2017.
(2) Guidance documents include the "National Functional Guidelines for Inorganic Superfund Methods Data Review," dated September 2016 and January 2017.

QAPP Worksheet #37: Data Usability Assessment
(UFP-QAPP Section 5.2.3)

Personnel (organization and position/title) responsible for participating in data usability assessment: GF quality manager in consultation with EPA work assignment manager.

Description of Data Usability Assessment Documentation

Quarterly data validation reports will be submitted with the annual reports to document data usability.

Project Objectives and Sampling Design

Project objectives and sampling design were agreed on previously. EPA Region 5, WDNR, and GF will use the data to document the quality of groundwater at and downgradient of NPI, support the shutdown of the groundwater extraction wells and cascade aerators used as interim remedial measures onsite and abandonment of monitoring wells, provide results for quarterly and annual discharge monitoring reports to the WDNR as needed, track NPI VOC levels at the ECMWF, monitor the performance of three SVE systems, and ultimately provide a basis for delisting of the site.

Data Verification and Data Validation Outputs

Quarterly verification assessments and validation reports will be submitted with the annual reports to document data usability. Any limitations of data usability, including trends, relationships, and anomalies will be described.

Assumptions and Implementation of the Selected Statistical Method

The selected statistical method is to use trend plots to evaluate the data. Assumptions include linear relationship, multivariate normality, no or little multicollinearity, and no autocorrelation. To date, the agencies have accepted the data trends and appear satisfied with NPI's progress.

FIGURES

No.	REVISIONS	DATE	BY
0	PRELIMINARY DRAFT.	06/28/17	CJP
1	FIRST DRAFT.	06/28/17	CJP
2	SECOND DRAFT.	07/13/17	CJP
3	THIRD DRAFT.	09/25/17	MCM

AREA SITE PLAN WITH WELL AND 1993 PLUME LOCATIONS

NATIONAL PRESTO INDUSTRIES, INC. AND EAU CLAIRE MUNICIPAL WELL FIELD

EAU CLAIRE, WISCONSIN

Gannett Fleming

HARRISBURG, PENNSYLVANIA — MADISON, WISCONSIN

PROJECT

QAPP FOR GROUNDWATER AND SVE SYSTEM MONITORING
NATIONAL PRESTO INDUSTRIES, INC.
EAU CLAIRE, WISCONSIN

TITLE

WATERTABLE GROUNDWATER CONTOUR MAP (JUNE 2016) WITH 1993 PLUME LOCATIONS

Gannett Fleming

HARRISBURG, PENNSYLVANIA — MADISON, WISCONSIN

DRAWN BY: CJP	SCALE: 1" = 700'
DESIGNED BY: CJP	PROJECT No.: 34283.000
APPROVED BY: CCW	DRAWING NO.: FIGURE 1
DATE: SEPTEMBER 2017	

092517
ccw_I34283-000_2017_01QA_F01

0 350' 700' 1400'

LEGEND

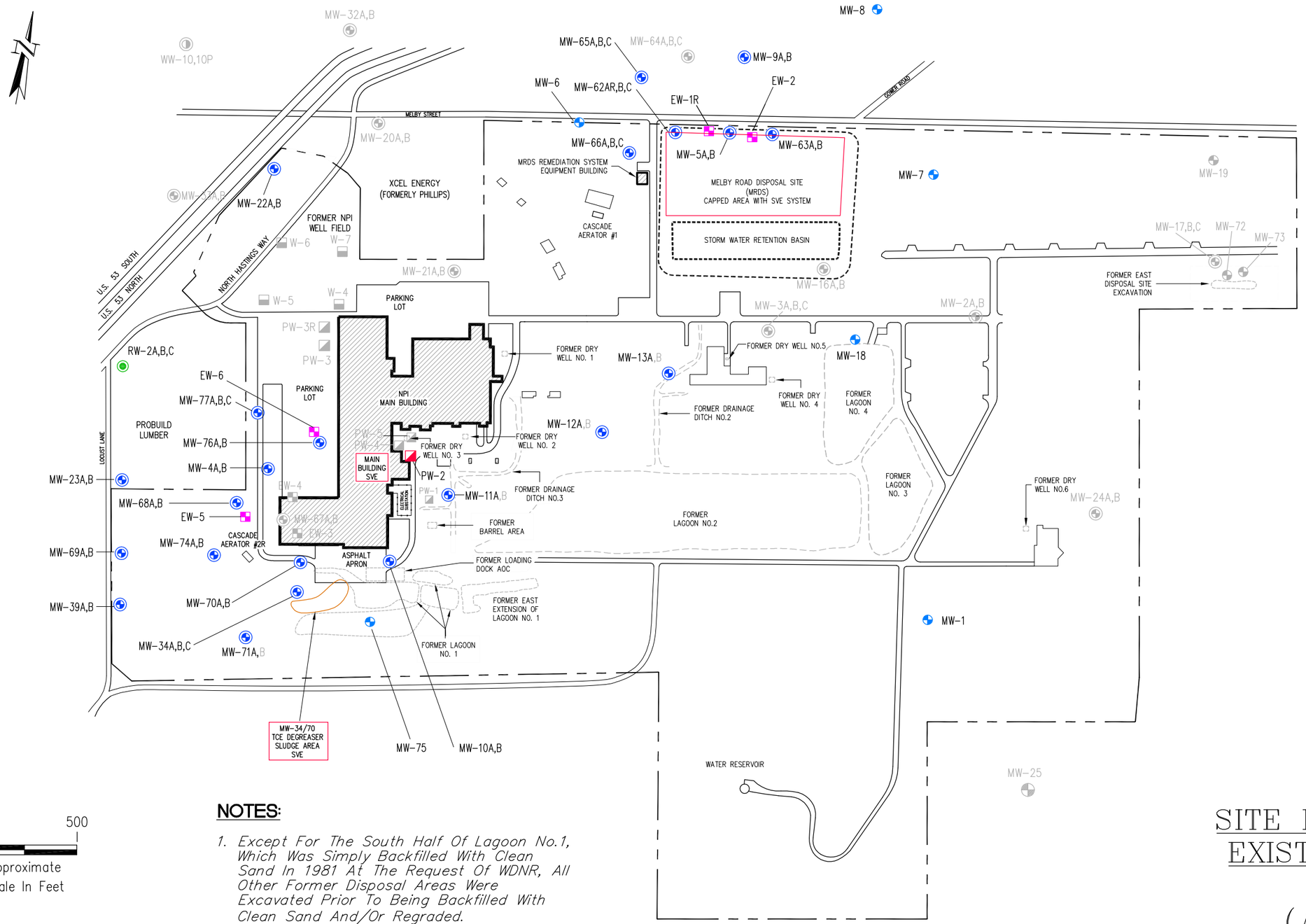
- 815 — Groundwater Contour (Dashed Where Inferred)
- Flow Direction
- (816.33) Groundwater Elevation At Well (Feet Above Mean Sea Level)
- MW-10A,B Nested Well Identification (Blue Underlined Well Source Of GWE Measurement)
- 1993 TCE Plume (Approximate)
- Eau Claire Production Well (Active Wells)
- Eau Claire Monitoring Well (Monitored by City, EC Prefix)
- WDNR Monitoring Well Nest (WW Prefix)
- WDNR Monitoring Well (WW Prefix)
- USEPA Monitoring Well (RW Prefix)
- USEPA Monitoring Well Nest (RW Prefix)
- NPI Superfund Monitoring Well Nest (MW Prefix)
- NPI Superfund Monitoring Well (MW Prefix)
- NPI LUST Monitoring Well (PW Prefix)
- NPI Superfund Extraction Well (EW Prefix)

NOTES

1. Groundwater Elevations Measured In Wells While EW-6 Was Pumping, And The Data From EW-1R, EW-5, MW-4A, and RW-15 Were Not Used To Develop The Contour Map.
2. Contours Above 830 Are Shown At 2-Foot Intervals And Contours Below 830 Are Shown At 1-Foot Intervals, Except As Shown Around EW-6.
3. Shaded Wells Have Been Abandoned.

Gannett Fleming

FIGURE 2



LEGEND

- *Individual Areas With Existing SVE Systems*
- MW-63A,B — *Nested Well Identification*
- *USEPA Monitoring Well Nest (RW Prefix)*
- *NPI Superfund Monitoring Well Nest (MW Prefix)*
- *NPI Superfund Monitoring Well (MW Prefix)*
- *NPI LUST Monitoring Well (PW Prefix)*
- *NPI Superfund Extraction Well (EW Prefix)*
- *Footprint Of Former On-Site Building*
- *NPI Property Line*

0 500

Approximate Scale In Feet

NOTES:

1. *Except For The South Half Of Lagoon No.1, Which Was Simply Backfilled With Clean Sand In 1981 At The Request Of WDNR, All Other Former Disposal Areas Were Excavated Prior To Being Backfilled With Clean Sand And/Or Regraded.*
2. *Shaded Wells Have Been Abandoned And Shaded Buildings Have Been Demolished And Removed.*

SITE PLAN WITH THREE EXISTING SVE SYSTEM LOCATIONS (AUGUST 2017)

NATIONAL PRESTO INDUSTRIES, INC.
EAU CLAIRE, WISCONSIN

082517
ccw_R34283-000_2017_01QA_F02

TABLES

NATIONAL PRESTO INDUSTRIES, INC.
EAU CLAIRE, WISCONSIN

TABLE 1

WELL CONSTRUCTION INFORMATION

Well/Piezometer ID (description/comment)	Plume	Grid Coord.	FN	Drilling Method	Completion Date or Year	Screened Interval (ft bgs)	Screened In (description of material)	Casing Dia-meter (inches)	Well Top Type	Casing/ Screen Material	Top of Casing Elevation (ft MSL)	Date of Abandonment
CW-10 (city production well)	1/2	B8		CT	1945	65-95	Gravel	20		Bronze	--	NA
CW-11	1/2	B8		CT	1947	56-90	Gravel	20		Bronze	--	NA
CW-14	1/2	B8		CT	1968	63-99	Gravel packed	16		SS	--	NA
CW-15	1/2	B8		CT	1968	62-87	Gravel packed	16		SS	--	NA
CW-16	1/2	B8		CT	1975	75-110	Gravel	20		SS	--	NA
CW-17	1/2	B8		CT	1975	65-100	Gravel	20		SS	--	NA
CW-19	1/2	B7		CT	1992	72-97	Gravel	20		SS	--	NA
CW-22	1/2	C7		CT	2017	54-100	Gravel	20		SS	--	NA
CW-23	1/2	B7		CT	2017	55-80	Gravel	20		SS	--	NA
EC-1 (city monitoring well)	1/2	C7		--	12/16/82	90-100	--	4	P	Steel	813.95	NA
EC-2	1/2	C7		--	12/20/82	18-28	--	4	P	Steel	814.44	NA
EC-3	1/2	A8		--	12/23/82	53-75	--	6	P	Steel	799.58	09/04/08
EC-4	1/2	A8		--	01/31/83	9-19	--	4	P	Steel	800.84	09/04/08
EC-5	1/2	C7		--	12/23/82	17-27	--	4	P	Steel	813.56	NA
EC-6	1/2	C7		--	01/04/83	15-25	--	4	P	Steel	813.19	NA
EC-7 (approved for abandonment-kept by city)	1/2	B6		--	01/05/83	19-29	--	4	P	Steel	816.22	NA
EC-8	1/2	A7		--	01/07/83	20-30	--	4		Steel	812.93	09/04/08
EW-1 (fka MW-14)	3/4	L6	1	AR	03/05/87	62.5-97.5	Alluvium	5		Steel	896.00	08/25/95
EW-1R (replaced EW-1)	3/4	L6		HSA/CT	08/25/95	75-100	Alluvium	6	F	SS	900.08	NA
EW-2 (fka MW-15)	3/4	L6		AR	02/26/87	69-104	Alluvium	8	F	Steel	901.45	NA
EW-3 (Last sampled 7/22/03)	1/2	K8		MR	09/01/92	65.2-85.2	Alluvium	6	Vault	Steel	897.22	06/24/10
EW-4	1/2	K7		MR	09/03/92	72-92	Alluvium	6	Vault	Steel	898.23	10/14/10
EW-5	1/2	K7		MR	07/10/03	70-90	Alluvium	6	Vault	Steel/SS	889.90	NA
EW-6	1/2	K7		Sonic	08/06/11	70.3-100.3	Alluvium	6	Vault	Steel/SS	894.89	NA
MW-1	3/4	M8	2	HSA	10/26/76	39.5-49.5	Alluvium	2	P	PVC	910.26	NA
MW-2A	3/4	M7	2,4	HSA	10/27/76	45-55	Bedrock	2		PVC	905.19	07/15/88
MW-2B	3/4	M7	2	HSA	10/27/76	6-16	Alluvium	2		PVC	905.19	07/15/88
MW-3A	3/4	L7	2,4	HSA	10/28/76	69-72	Bedrock	2		PVC	899.95	07/15/88
MW-3B	3/4	L7	2,4	HSA	10/28/76	73-76	Bedrock	2		PVC	899.95	07/15/88
MW-3C	3/4	L7	2,4	HSA	10/28/76	77-80	Bedrock	2		PVC	899.95	07/15/88
MW-4A	1/2	K7	2	HSA	10/28/76	70-80	Alluvium	2	P	PVC	898.42	NA
MW-4B	1/2	K7		MR	05/24/90	95-105	Alluvium	2	P	PVC	894.39	NA
MW-5A	3/4	L6	2	HSA	02/27/84	64-81	Alluvium	2	P	PVC	902.60	NA
MW-5B	3/4	L6	2	MR	12/05/86	87-97	Alluvium	2	P	PVC	902.39	NA
MW-6	3/4	L6	2	HSA	01/10/85	73.8-88.8	Alluvium	2	P	PVC	904.70	NA
MW-7	3/4	M6	2,4	MR	01/08/85	62-77	Bedrock	2	P	PVC	897.73	NA
MW-8	3/4	M6	2	HSA	01/11/85	75-90	Alluvium	2	P	PVC	904.24	NA
MW-9A	3/4	L6	2	MR	03/28/85	80-90	Alluvium	2	P	PVC	905.30	NA
MW-9B	3/4	L6	2,4	HSA	03/28/85	98-113	Bedrock	2	P	PVC	905.30	NA
MW-10A	1/2	K8	4	HSA	11/14/86	56-71	Both	2	P	PVC	894.84	NA
MW-10B	1/2	K8	4	MR	11/14/86	90.5-100.5	Bedrock	2	P	PVC	894.91	NA
MW-11A	1/2	K7		HSA	11/15/86	58-73	Alluvium	2	P	PVC	896.03	NA
MW-11B	1/2	K7	4	MR	11/17/86	77-87	Bedrock	2	P	PVC	896.27	11/23/11
MW-12A	1/2	L7		HSA	11/18/86	58-73	Alluvium	2	P	PVC	897.09	NA
MW-12B	1/2	L7	4	MR	11/18/86	77.5-87.5	Bedrock	2	P	PVC	897.20	11/23/11
MW-13A	3/4	L7		HSA	11/21/86	58.5-73.5	Alluvium	2	P	PVC	896.86	NA
MW-13B	3/4	L7	4	HAS	11/21/86	81-91	Bedrock	2	P	PVC	?	11/23/11
MW-14 (nka EW-1)	3/4	L6	1	AR	03/05/87	62.5-97.5	Alluvium	2		Steel	896.00	03/05/87

TABLE 1

WELL CONSTRUCTION INFORMATION

Well/Piezometer ID (description/comment)	Plume	Grid Coord.	FN	Drilling Method	Completion Date or Year	Screened Interval (ft bgs)	Screened In (description of material)	Casing Dia-meter (inches)	Well Top Type	Casing/ Screen Material	Top of Casing Elevation (ft MSL)	Date of Abandonment
MW-15 (nka EW-2)	3/4	L6		AR	02/26/87	69-104	Alluvium	2		Steel	895.81	02/26/87
MW-16A	3/4	M7	4	HSA	11/25/86	58-73	Bedrock	2		PVC	896.62	08/21/98
MW-16B	3/4	M7	4	MR	11/24/86	83.5-93.5	Bedrock	2		PVC	896.51	08/21/98
MW-17	5	N7	4	HSA	12/03/86	25-40	Both	2	P	PVC	898.91	11/23/11
MW-17B	5	N7	4	HSA	12/04/86	50-60	Bedrock	2	P	PVC	899.12	11/23/11
MW-17C	5	N7	4	MR	05/20/88	70-80	Bedrock	2	P	PVC	899.50	11/23/11
MW-18	3/4	M7	4	HSA	05/19/88	58-73	Bedrock	2	P	PVC	898.38	NA
MW-19	5	N6	4	HSA	05/17/88	58-73	Bedrock	2	P	PVC	898.89	11/30/11
MW-20A	3/4	K6		HSA	05/25/88	65.5-80.5	Alluvium	2		PVC	897.82	04/15/95
MW-20B	3/4	K6		HSA	06/01/88	92-102	Alluvium	2		PVC	896.74	04/15/95
MW-21A	3/4	K7		HSA	05/23/88	67-82	Alluvium	2		PVC	899.27	04/07/10
MW-21B	3/4	K7		MR	05/20/88	92-102	Alluvium	2		PVC	898.95	04/07/10
MW-22A	3/4	K6		HSA	06/03/88	66.5-81.5	Alluvium	2	P	PVC	900.79	NA
MW-22B	3/4	K6		HSA	06/01/88	91.5-101.5	Alluvium	2	P	PVC	900.75	NA
MW-23A	1/2	J7		HSA	06/04/88	65-80	--	2	P	PVC	895.99	NA
MW-23B	1/2	J7		HSA	06/03/88	90-100	--	2	P	PVC	895.95	NA
MW-24A	3/4	M7	4	MR	05/25/88	45-60	Bedrock	2		PVC	915.66	09/05/08
MW-24B	3/4	M7	4	MR	05/23/88	70-80	Bedrock	2		PVC	915.57	09/05/08
MW-25	3/4	M8	4	HSA	05/17/88	39-54	Both	2		PVC	930.35	09/05/08
MW-26A	3/4	L5		HSA	06/22/89	63-78	Alluvium	2	F	PVC	890.17	NA
MW-26B	3/4	L5		MR	06/20/89	109-119	Alluvium	2	F	PVC	890.03	NA
MW-27A	3/4	L5		HSA	06/21/89	62-77	Alluvium	2	F	PVC	890.20	NA
MW-27B	3/4	L5		MR	06/20/89	85.3-95.3	Alluvium	2	F	PVC	890.15	NA
MW-28A	3/4	L4		HSA	06/08/89	65-80	Alluvium	2		PVC	892.86	06/15/99
MW-28B	3/4	L4		MR	06/08/89	113-123	Alluvium	2		PVC	893.16	06/15/99
MW-29A	3/4	L3		HSA	05/25/89	69-84	Alluvium	2	P	PVC	892.72	NA
MW-29B	3/4	L3		MR	05/31/89	124-134	Alluvium	2	P	PVC	892.49	NA
MW-30A	5	M5		HSA	06/12/89	66-81	Alluvium	2		PVC	898.69	09/08/08
MW-30B	5	M5		MR	06/10/89	115-125	Alluvium	2		PVC	898.49	09/08/08
MW-31	1/2	J6		HSA	06/02/89	56-71	Alluvium	2		PVC	887.65	09/09/08
MW-32A	3/4	K6		HSA	06/23/89	59-74	Alluvium	2		PVC	887.83	04/08/95
MW-32B	3/4	K6		MR	06/21/89	90-100	Alluvium	2		PVC	887.77	04/08/95
MW-33A	1/2	J6		HSA	07/07/89	55-70	Alluvium	2		PVC	885.30	04/07/10
MW-33B	1/2	J6		MR	07/07/89	100-110	Alluvium	2		PVC	885.25	04/07/10
MW-34A (data per boring log)	1/2	K8		HSA	06/08/90	67-72	Alluvium	2	P	PVC	895.36	NA
MW-34B (data per boring log)	1/2	K8	4	MR	05/31/90	90-100	Both	2	P	PVC	895.28	NA
MW-34C	1/2	K8	4	--	--	?-102	Bedrock	2	P	PVC	895.25	NA
MW-35A	1/2	I7		HSA	05/31/90	59-74	Alluvium	2	P	PVC	888.28	NA
MW-35B	1/2	I7		MR	06/06/90	84-94	Alluvium	2	P	PVC	888.02	NA
MW-36A	1/2	I7		HSA	06/06/90	63.5-78.5	Alluvium	2	F	PVC	889.87	11/23/11
MW-36B	1/2	I7		MR	06/07/90	88.5-98.5	Alluvium	2	F	PVC	889.89	11/23/11
MW-37A	1/2	I7		HSA	12/18/90	55.7-70.7	Alluvium	2	F	PVC	885.55	NA
MW-37B	1/2	I7		HSA	02/12/91	68.5-73.5	Alluvium	2	F	PVC	885.27	NA
MW-38A	1/2	I8		HSA	12/16/90	54.5-69.5	Alluvium	2	F	PVC	884.89	NA
MW-38B	1/2	I8		HSA	02/05/91	97.5-107.5	Alluvium	2	F	PVC	884.82	NA
MW-38C	1/2	I8		MR	01/13/91	139.2-149.2	Alluvium	2	F	PVC	884.83	NA
MW-39A	1/2	J8		HSA	12/11/90	62.5-77.5	Alluvium	2	P	PVC	896.17	NA
MW-39B	1/2	J8		MR	01/26/91	114.8-124.8	Alluvium	2	P	PVC	896.38	11/29/11
MW-40A	1/2	H7		HSA	12/20/90	58-73	Alluvium	2		PVC	886.57	08/24/09
MW-40B	1/2	H7		MR	01/16/91	79-89	Alluvium	2		PVC	886.34	08/24/09
MW-41A	1/2	H8		HSA	12/19/90	56-71	Alluvium	2	F	PVC	884.04	NA
MW-41B	1/2	H8		MR	01/23/91	102.5-112.5	Alluvium	2	F	PVC	883.84	NA

TABLE 1

WELL CONSTRUCTION INFORMATION

Well/Piezometer ID (description/comment)	Plume	Grid Coord.	FN	Drilling Method	Completion Date or Year	Screened Interval (ft bgs)	Screened In (description of material)	Casing Dia-meter (inches)	Well Top Type	Casing/ Screen Material	Top of Casing Elevation (ft MSL)	Date of Abandonment
MW-42A	1/2	G7		HSA	01/31/91	65.5-75.5	Alluvium	2	P	PVC	891.83	11/29/11
MW-42B	1/2	G7		MR	01/17/91	74.5-84.5	Alluvium	2	P	PVC	891.32	11/29/11
MW-43A	1/2	H7		HSA	02/12/91	61-76	Alluvium	2	F	PVC	885.34	NA
MW-43B	1/2	H7		MR	02/11/91	107.5-117.5	Alluvium	2	F	PVC	885.35	NA
MW-44A	1/2	F6		HSA	08/20/91	62-67	Alluvium	2	F	PVC	885.35	08/25/15
MW-44B	1/2	F6		HSA	08/24/91	114-124	Alluvium	2	F	PVC	885.34	08/25/15
MW-45A	1/2	F6		HSA	08/21/91	63-78	Alluvium	2	F	PVC	886.20	NA
MW-45B	1/2	F6		MR	09/11/91	101-111	Alluvium	2	F	PVC	886.26	NA
MW-45C	1/2	F6		MR	08/26/91	134-144	Alluvium	2	F	PVC	886.05	NA
MW-46A (not found)	1/2	G7		HSA	08/22/91	60-75	Alluvium	2	P	PVC	885.46	NA
MW-46B (not found)	1/2	G7		MR	09/12/91	99.5-109.5	Alluvium	2	P	PVC	885.42	NA
MW-46C (not found)	1/2	G7		MR	08/28/91	134.3-144.3	Alluvium	2	P	PVC	885.38	NA
MW-47A	1/2	G7		HSA	08/23/91	60-75	Alluvium	2	P	PVC	888.39	NA
MW-47B	1/2	G7		MR	09/04/91	100-110	Alluvium	2	P	PVC	888.24	NA
MW-48A	1/2	E6		HSA	09/07/91	66.5-81.5	Alluvium	2	F	PVC	885.15	12/01/11
MW-48B	1/2	E6		MR	09/06/91	93-103	Alluvium	2	F	PVC	885.40	12/01/11
MW-49A	1/2	D6		HSA	09/10/91	78.5-91.5	Alluvium	2	F	PVC	883.04	NA
MW-49B	1/2	D6		MR	09/09/91	107-117	Alluvium	2	F	PVC	883.02	NA
MW-50A (not found)	1/2	F6		HSA	09/16/91	63.4-78.4	Alluvium	2	F	PVC	883.61	NA
MW-50B (not found)	1/2	F6		MR	09/15/91	95-105	Alluvium	2	F	PVC	883.57	NA
MW-51A	1/2	F6		HSA	09/17/91	63.5-78.5	Alluvium	2	F	PVC	884.02	NA
MW-51B	1/2	F6		MR	09/17/91	102-112	Alluvium	2	F	PVC	883.99	NA
MW-52A	1/2	F6		HSA	10/02/91	67.4-82.4	Alluvium	2	F	PVC	884.13	NA
MW-52B	1/2	F6		MR	10/02/91	113-123	Alluvium	2	F	PVC	884.12	NA
MW-53A	1/2	E6		HSA	10/05/91	76-91	Alluvium	2	F	PVC	887.93	NA
MW-53B	1/2	E6		MR	10/05/91	112-123	Alluvium	2	F	PVC	888.25	NA
MW-54A	1/2	D6		HSA	10/10/91	77-92	Alluvium	2	F	PVC	883.78	NA
MW-54B	1/2	D6		MR	10/11/91	112-122	Alluvium	2	F	PVC	883.87	NA
MW-54C	1/2	D6		MR	10/09/91	142-152	Alluvium	2	F	PVC	883.66	NA
MW-55A	1/2	D6		HSA	11/05/91	78-93	Alluvium	2	F	PVC	881.75	NA
MW-55B	1/2	D6		MR	11/26/91	118.5-128.5	Alluvium	2	F	PVC	882.08	NA
MW-55C	1/2	D6		MR	11/04/91	154-164	Alluvium	2	F	PVC	881.91	NA
MW-56A	1/2	E5		HSA	11/06/91	75.5-90.5	Alluvium	2		PVC	885.67	09/04/08
MW-56B	1/2	E5		MR	11/11/91	150-160	Alluvium	2		PVC	885.89	09/04/08
MW-57A	1/2	E6		HSA	11/23/91	76-91	Alluvium	2	F	PVC	886.31	NA
MW-57B	1/2	E6		MR	11/21/91	108-118	Alluvium	2	F	PVC	886.13	NA
MW-58A	1/2	D6		HSA	11/07/91	76-91	Alluvium	2	F	PVC	880.88	?
MW-58B	1/2	D6		MR	11/13/91	112-122	Alluvium	2	F	PVC	880.96	12/01/11
MW-59A (approved for abandonment, but can't find)	1/2	F6		HSA	11/08/91	62-77	Alluvium	2		PVC	882.00	NA
MW-59B (approved for abandonment, but can't find)	1/2	F6		MR	11/19/91	129-139	Alluvium	2		PVC	882.07	NA
MW-60A	1/2	D7		HSA	12/04/91	78.5-93.5	Alluvium	2	F	PVC	879.19	NA
MW-60B	1/2	D7		MR	12/08/91	104-114	Alluvium	2	F	PVC	879.09	NA
MW-61A	1/2	C6		HSA	12/05/91	78.5-93.5	Alluvium	2	F	PVC	879.37	NA
MW-61B	1/2	C6		MR	12/11/91	124-134	Alluvium	2	F	PVC	879.58	NA
MW-62A	3/4	L6		HSA	06/25/92	61-76	Alluvium	2		PVC	893.69	12/22/98
MW-62AR	3/4	L6		HSA	12/22/98	71-86	Alluvium	2	P	PVC	901.75	NA
MW-62B	3/4	L6		MR	06/30/92	96-106	Alluvium	2	P	PVC	901.79	NA
MW-62C	3/4	L6		MR	06/24/92	126.5-136.5	Alluvium	2	P	PVC	901.15	NA
MW-63A	3/4	M6		HSA	06/28/92	65-80	Alluvium	2	P	PVC	899.05	NA
MW-63B	3/4	M6		MR	06/27/92	95-105	Alluvium	2	P	PVC	899.13	NA

TABLE 1

WELL CONSTRUCTION INFORMATION

Well/Piezometer ID (description/comment)	Plume	Grid Coord.	FN	Drilling Method	Completion Date or Year	Screened Interval (ft bgs)	Screened In (description of material)	Casing Dia-meter (inches)	Well Top Type	Casing/ Screen Material	Top of Casing Elevation (ft MSL)	Date of Abandonment
MW-64A	3/4	L6		HSA	07/08/92	63.5-78.5	Alluvium	2	P	PVC	894.89	05/08/14
MW-64B	3/4	L6		MR	07/08/92	103.8-113.8	Alluvium	2	P	PVC	895.24	05/08/14
MW-64C	3/4	L6		MR	07/01/92	139-149	Alluvium	2	P	PVC	894.75	05/08/14
MW-65A	3/4	L6		HSA	07/02/92	60.4-75.4	Alluvium	2	P	PVC	891.68	NA
MW-65B	3/4	L6		MR	07/08/92	100-110	Alluvium	2	P	PVC	891.62	NA
MW-65C	3/4	L6		MR	07/07/92	133.9-143.9	Alluvium	2	P	PVC	891.77	NA
MW-66A	3/4	L6		HSA	06/27/92	66.5-81.5	Alluvium	2	P	PVC	900.53	NA
MW-66B	3/4	L6		MR	07/01/92	111-121	Alluvium	2	P	PVC	900.26	NA
MW-66C	3/4	L6		MR	06/27/92	150-160	Alluvium	2	P	PVC	900.43	NA
MW-67A	1/2	K7		HSA	06/22/92	61-76	Alluvium	2		PVC	895.96	09/22/10
MW-67B	1/2	K7		MR	07/09/92	77.8-82.8	Alluvium	2		PVC	895.79	09/22/10
MW-68A	1/2	J7		HSA	07/08/92	63.5-78.5	Alluvium	2	P	PVC	896.47	NA
MW-68B	1/2	J7		MR	06/19/92	97-107	Alluvium	2	P	PVC	896.77	NA
MW-69A	1/2	J8		HSA	07/09/92	65-80	Alluvium	2	P	PVC	898.02	NA
MW-69B	1/2	J8		MR	06/21/92	108.8-118.8	Alluvium	2	P	PVC	898.23	NA
MW-70A	1/2	K8		HSA	06/22/92	62-77	Alluvium	2	P	PVC	895.68	NA
MW-70B	1/2	K8		HSA	07/10/92	77-82	Alluvium	2	P	PVC	895.67	NA
MW-71A	1/2	K8		MR	06/17/92	57-72	Alluvium	2	P	PVC	894.70	NA
MW-71B	1/2	K8	4	MR	07/09/92	79-89	Both	2	P	PVC	894.89	11/23/11
MW-72	5	N7		HSA	09/09/98	34-49	Both	2	P	PVC	899.26	11/23/11
MW-73	5	N7		HSA	09/09/98	32-47	Both	2	P	PVC	899.71	11/23/11
MW-74A	1/2	J8		HSA	07/08/03	66-76	Alluvium	2	P	PVC	896.08	NA
MW-74B	1/2	J8	4	MR	07/09/03	95-100	Bedrock	2	P	PVC	895.88	NA
MW-75	1/2	K8	4	HSA	07/11/03	56-66	Bedrock	2	P	PVC	890.61	NA
MW-76A	1/2	K7		Sonic	09/22/10	65-80	Alluvium	2	F	PVC	894.80	NA
MW-76B	1/2	K7		Sonic	09/22/10	95-100	Alluvium	2	F	PVC	895.12	NA
MW-77A	1/2	K7		Sonic	09/22/10	65-80	Alluvium	2	F	PVC	895.22	NA
MW-77B	1/2	K7		Sonic	09/21/10	95-100	Alluvium	2	F	PVC	895.21	NA
MW-77C	1/2	K7		Sonic	09/21/10	115-120	Alluvium	2	F	PVC	895.18	NA
PW-1	1/2	K7		HSA	01/05/94	65-75	Alluvium	2		PVC	898.28	09/08/08
PW-2 (approved for aband.-kept for WL measurements)	1/2	K7		HSA	01/03/94	66-76	Alluvium	2		PVC	894.71	NA
PW-3	1/2	K7		HSA	07/12/94	69-79	Alluvium	2		PVC	898.83	06/15/96
PW-3R	1/2	K7		HSA	11/22/96	69-79	Alluvium	2	F	PVC	896.21	08/18/17
PW-4	1/2	K7		HSA	07/12/97	68-78	Alluvium	2		PVC	895.59	09/08/08
PW-5	1/2	K7		HSA	07/13/94	67-77	Alluvium	2		PVC	886.93	01/15/04
PW-67 (Owner: Joles)	5	M4		--	--	--	--	--		--	--	NA
PW-218 (Owner: Martens)	5	M4		--	--	--	--	--		--	--	NA
PW-230 (Owner: Ihlenfeld)	5	M4		--	--	--	--	--		--	--	NA
RW-1	1/2	F7		HSA	12/12/85	60.5-112.5	Alluvium	2		PVC	887.19	07/27/09
RW-2A	1/2	J7		HSA	01/03/86	69-79	Alluvium	2	P	PVC	897.18	NA
RW-2B	1/2	J7		HSA	01/04/86	91-101	Alluvium	2	P	PVC	896.78	NA
RW-2C	1/2	J7		HSA	12/15/85	108-118	Alluvium	2	P	PVC	897.57	NA
RW-3A	1/2	C6		HSA	12/19/85	79-89	Alluvium	2	P	PVC	881.78	NA
RW-3B	1/2	C6		HSA	01/07/86	96-106	Alluvium	2	P	PVC	881.48	NA
RW-3C	1/2	C6		HSA	01/05/86	108.5-118.5	Alluvium	2	P	PVC	881.30	NA
RW-4	1/2	H9	4	HSA	02/04/86	53-78	Both	2		PVC	884.65	09/10/08
RW-5 (approved for abandonment, but can't find)	1/2	D8		HSA	01/18/86	82-112	Alluvium	2		PVC	882.19	NA
RW-6	1/2	D7	4	HSA	02/11/86	78.5-103.5	Both	2		PVC	883.89	09/03/08
RW-7	1/2	H6		HSA	01/29/86	68-118	Alluvium	2		PVC	890.71	09/10/08
RW-8	1/2	G5		HSA	02/05/86	64-109	Alluvium	2		PVC	889.12	09/09/08

TABLE 1

WELL CONSTRUCTION INFORMATION

Well/Piezometer ID (description/comment)	Plume	Grid Coord.	FN	Drilling Method	Completion Date or Year	Screened Interval (ft bgs)	Screened In (description of material)	Casing Dia-meter (inches)	Well Top Type	Casing/ Screen Material	Top of Casing Elevation (ft MSL)	Date of Abandonment
RW-9	1/2	D4		HSA	01/20/86	75.5-105.5	Alluvium	2		PVC	886.62	09/10/08
RW-10	1/2	D6		HSA	07/21/87	70-120	Alluvium	2		PVC	888.28	09/04/08
RW-11	1/2	E5		HSA	07/21/87	65-120	Alluvium	2		PVC	890.45	09/03/08
RW-12	1/2	F6		HSA	07/22/87	60-120	Alluvium	2		PVC	891.01	07/27/09
RW-13	1/2	F8	4	HSA	08/11/87	65-75	Bedrock	2		PVC	885.57	09/03/08
RW-14	1/2	H7		HSA	07/24/87	54-114	Alluvium	2		PVC	888.06	07/27/09
RW-15	1/2	J7		HSA	07/24/87	52-92	Alluvium	2	P	PVC	874.76	NA
RW-16	1/2	G7		HSA	07/28/87	63-73	Alluvium	2	P	SS	888.87	NA
RW-16B	1/2	G7		HSA	02/06/91	103-113	Alluvium	2	P	PVC	889.66	NA
RW-16C	1/2	G7		MR	01/31/91	142.5-152.5	Alluvium	2	P	PVC	890.01	NA
RW-17 (approved for abandonment, but can't find)	1/2	G7		HSA	07/29/87	60-70	Alluvium	2		SS	890.24	NA
RW-18 (PW-6 on Indianhead property?)	--	--	3	HSA	07/29/87	62-72	Alluvium	2		SS	890.62	Unknown
RW-19	1/2	G7		HSA	07/30/87	60-70	Alluvium	2	P	SS	888.57	12/01/11
RW-20	1/2	G7		HSA	07/30/87	64-74	Alluvium	2		SS	889.43	05/15/95
RW-21	1/2	G6		HSA	07/31/87	63-73	Alluvium	2		SS	890.39	02/15/95
RW-22	1/2	G7		HSA	07/31/87	62-72	Alluvium	2	P	SS	887.42	12/01/11
RW-23 (not found)	1/2	H7		HSA	07/31/87	61-71	Alluvium	2		SS	890.30	NA
RW-24	1/2	E6		HSA	08/01/87	66-76	Alluvium	2		SS	886.52	09/04/08
RW-25 (approved for abandonment, but can't find)	1/2	G3	4	HSA	08/13/87	55-65	Bedrock	2		PVC	926.22	NA
WW-1	--	--		HSA	08/08/85	30-40	--	2		PVC	945.05	10/16/01
WW-2	--	--		HSA	08/10/85	57.5-67.5	--	2		PVC	900.53	NA
WW-3	3/4	K5		HSA	07/27/85	63.2-73.2	--	2		PVC	891.45	12/12/91
WW-3B	3/4	K5		MR	06/19/89	138.5-148.5	Alluvium	2		PVC	888.98	12/12/91
WW-4	--	--		HSA	08/07/85	70-80	--	2		PVC	904.18	07/26/06
WW-5	3/4	K4		HSA	08/01/85	69-79	--	2		PVC	892.55	09/09/08
WW-5P	3/4	K4		HSA	10/01/85	104-109	--	2		PVC	892.69	09/09/08
WW-6	1/2	I6		HSA	07/31/85	57.8-67.8	--	2		PVC	889.46	09/09/08
WW-7	1/2	I4		HSA	08/08/85	15-25	--	2		PVC	893.19	09/08/08
WW-8	3/4	J2		HSA	08/01/85	16.75-26.75	--	2		PVC	846.94	09/08/08
WW-9	3/4	N3		HSA	08/06/85	74.9-84.9	--	2		PVC	901.71	08/19/99
WW-9P	3/4	N3		HSA	07/25/85	105-115	--	2		PVC	901.63	08/19/99
WW-10	3/4	J6		HSA	10/02/85	60-70	--	2		PVC	889.10	05/07/99
WW-10P	3/4	J6		HSA	10/02/85	91.3-96.3	--	2		PVC	889.19	05/07/99
WW-11	5	N6		HSA	09/26/85	36.5-46.5	--	2		PVC	901.36	09/05/08
WW-11P	5	N6		HSA	09/30/85	72-77	--	2		PVC	901.16	09/05/08
WW-12 (not found)	3/4	J4		HSA	09/27/85	17-27	--	2		PVC	892.25	NA
WW-13	4	L5		HSA	10/01/85	67-77	--	2	P	PVC	905.45	11/29/11
WW-14	5	O4		HSA	05/07/85	70-80	--	2		PVC	899.72	09/10/08
WW-15	1/2	I8		HSA	10/03/85	53-63	Alluvium	2	P	PVC	882.61	NA
WW-15B	1/2	I8		HSA	02/06/91	95.6-105.6	Alluvium	2	F	PVC	879.97	11/23/11
WW-15C	1/2	I8		MR	02/01/91	137-147	Alluvium	2	F	PVC	879.76	11/23/11
WW-16	1/2	H8		HSA	10/02/86	57-67	--	2		PVC	885.63	09/10/08
WW-17	1/2	H5		HSA	10/01/85	13-23	--	2		PVC	887.21	09/08/08
WW-18	1/2	I5		HSA	10/01/85	16-26	--	2		PVC	890.84	09/08/08
WW-19	3/4	J3		HSA	09/28/85	20-30	--	2		PVC	894.02	11/30/11
Hallie Golf Course	110th Avenue			--	--	TD = 86	--	6.5		--	--	09/05/08
Don & Bonnie Berg	11265 16th Ave			--	--	TD = 73.4	--	4		--	--	09/09/08

TABLE 1

WELL CONSTRUCTION INFORMATION

NOTES:

Red font in the "Well/Piezometer ID" column indicates the well/piezometer is abandoned or lost/destroyed (109).

Purple font in the "Well/Piezometer ID" column indicates well is approved for abandonment (but 5 not found, EC-7 kept by City, and PW-2 kept for water level measurements).

Blue font in the "Plume" column indicates well not found (12).

Melby Rd. wells MW-62B/C and MW-5A/B and East Disposal Site wells MW-17A, MW-72, and MW-73 were resurveyed by Ayres in December 1998.

Site datum = Mean sea level (MSL)

AR = Air rotary

CT = Cable tool

CW = City production well

EC = City monitoring well

EW = NPI extraction well

F = Flush-mount well

FN = Footnote (see below)

HSA = Hollow stem auger

MR = Mud rotary

MW = NPI monitoring well

NA = Not abandoned

P = Pro top well

PW = NPI petroleum UST well

RW = EPA monitoring well

Screened Interval = Depth in feet below ground surface (ft bgs) of screened interval

SS = Stainless steel

WW = WDNR monitoring well

-- = Not available/unknown

FOOTNOTES:

(1) Converted to/replaced by EW-1R in August 1995.

(2) Pre-remedial investigation monitoring well.

(3) Well was lost/destroyed in year shown in "Date of Abandonment" column.

(4) Denotes a well screened in sandstone bedrock or both bedrock and alluvium (i.e., sand and gravel glacial outwash).

NATIONAL PRESTO INDUSTRIES, INC.
EAU CLAIRE, WISCONSIN

TABLE 2

GROUNDWATER AND PUMPED GROUNDWATER SAMPLING SCHEDULE

PLUME Grouping Sample ID	Grid ID/ Sample Location	Sampling Frequency		Comments
		NPI VOCs	Cadmium	
PLUME 1/2				
CW-11	B8	Quarterly	None	
CW-15	B8	Quarterly	None	
CW-16	B8	Quarterly	None	
CW-17	B8	Quarterly	None	
CW-19	B7	Quarterly	None	
CW-22	C7	Quarterly	None	
CW-23	B7	Quarterly	None	
Raw	Air stripper bldg	Quarterly	None	
Tower A	Air stripper bldg	Quarterly	None	
Tower B	Air stripper bldg	Quarterly	None	
Finished Product	Water plant	Quarterly	None	
EC-1	C7	Quarterly	None	
EC-2	C7	Annual	None	
EC-5	C7	Annual	None	
EC-6	C7	Annual	None	
EW-5	K7	Quarterly	Semi-annual	Shallow and deep samples are collected(1)
EW-6	K7	Quarterly	Semi-annual	
CAS-2R	K7	None	None	Use results from MH-18(2)
MH-18	K7	Quarterly	Annual	Expanded analyte list in Q4(3)
MW-4A	K7	Quarterly	Annual	
MW-4B	K7	Quarterly	Annual	
MW-10A	K8	None	Quarterly	
MW-10B	K8	None	Quarterly	
MW-11A	K7	None	None	
MW-12A	L7	None	None	
MW-23A	J7	Quarterly	None	
MW-23B	J7	Quarterly	None	
MW-34A	K8	Quarterly	Semi-annual	
MW-34B	K8	Quarterly	Semi-annual	
MW-34C	K8	Quarterly	Annual	
MW-35A	I7	Annual	None	
MW-35B	I7	Annual	None	
MW-37A	I7	None	None	
MW-37B	I7	Biennial	None	
MW-38A	I8	Annual	None	
MW-38B	I8	Semi-annual	None	
MW-38C	I8	Annual	None	
MW-39A	J8	None	None	
MW-41A	H8	Annual	None	
MW-41B	H8	Annual	None	
MW-43A	H7	Annual	None	
MW-43B	H7	Annual	None	

TABLE 2

GROUNDWATER AND PUMPED GROUNDWATER SAMPLING SCHEDULE

PLUME Grouping Sample ID	Grid ID/ Sample Location	Sampling Frequency		Comments
		NPI VOCs	Cadmium	
MW-45A	F6	Biennial	None	
MW-45B	F6	Semi-annual	None	
MW-45C	F6	Semi-annual	None	
MW-46A	G7	Lost	None	If found sample once for NPI VOCs and evaluate
MW-46B	G7	Lost	None	If found sample once for NPI VOCs and evaluate
MW-46C	G7	Lost	None	If found sample once for NPI VOCs and evaluate
MW-47A	G7	Biennial	None	
MW-47B	G7	Biennial	None	
MW-49A	D6	Annual	None	
MW-49B	D6	Annual	None	
MW-50A	F6	Lost	None	If found sample once for NPI VOCs and evaluate
MW-50B	F6	Lost	None	If found sample once for NPI VOCs and evaluate
MW-51A	F6	Biennial	None	
MW-51B	F6	Annual	None	
MW-52A	F6	Annual	None	
MW-52B	F6	Annual	None	
MW-53A	E6	Biennial	None	
MW-53B	E6	Annual	None	
MW-54A	D6	Biennial	None	
MW-54B	D6	Annual	None	
MW-54C	D6	Annual	None	
MW-55A	D6	None	None	
MW-55B	D6	Annual	None	
MW-55C	D6	Annual	None	
MW-57A	E6	Biennial	None	
MW-57B	E6	Biennial	None	
MW-59A	F6	Lost	None	If found sample once for NPI VOCs and evaluate
MW-59B	F6	Lost	None	If found sample once for NPI VOCs and evaluate
MW-60A	D7	Biennial	None	
MW-60B	D7	Biennial	None	
MW-61A	C6	Biennial	None	
MW-61B	C6	Biennial	None	
MW-68A	J7	Annual	Annual	
MW-68B	J7	Semi-annual	Quarterly	
MW-69A	J8	None	None	
MW-69B	J8	None	None	
MW-70A	K8	Quarterly	Annual	
MW-70B	K8	Quarterly	Quarterly	
MW-71A	K8	None	None	
MW-74A	J8	Annual	None	
MW-74B	J8	Annual	None	
MW-75	K8	None	Quarterly	
MW-76A	K7	Quarterly	None	
MW-76B	K7	Quarterly	None	
MW-77A	K7	Quarterly	None	
MW-77B	K7	Quarterly	None	

TABLE 2

GROUNDWATER AND PUMPED GROUNDWATER SAMPLING SCHEDULE

PLUME Grouping Sample ID	Grid ID/ Sample Location	Sampling Frequency		Comments
		NPI VOCs	Cadmium	
MW-77C	K7	Quarterly	None	
PW-2	K7	None	None	
PW-3R	K7	Annual	None	
RW-2A	J7	Semi-annual	None	
RW-2B	J7	Semi-annual	None	
RW-2C	J7	Semi-annual	None	
RW-3A	C6	Semi-annual	None	
RW-3B	C6	Semi-annual	None	
RW-3C	C6	Semi-annual	None	
RW-15	J7	Semi-annual	None	
RW-16	G7	Annual	None	
RW-16B	G7	Annual	None	
RW-16C	G7	Annual	None	
RW-18	H8	None	None	
RW-23	H7	Lost	None	If found sample once for NPI VOCs and evaluate
WW-15	I8	Annual	None	
PLUME 3/4				
EW-1R	L6	Quarterly	None	Shallow, mid-depth, and deep[1,4]
EW-2	L6	Quarterly	None	Shallow and deep[1,4]
CAS-1	L6	None	None	Quarterly sampling if EW-1R and/or EW-2 resume pumping
MW-1	M8	None	None	
MW-5A	L6	Semi-annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-5B	L6	Semi-annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-6	L6	Biennial	None	
MW-7	M6	None	None	Previously classified as a Plume 5 monitoring well
MW-8	M6	None	None	Previously classified as a Plume 5 monitoring well
MW-9A	L6	Biennial	None	
MW-9B	L6	None	None	
MW-13A	L7	None	None	
MW-18	M7	None	None	
MW-22A	K6	None	None	
MW-22B	K6	Biennial	None	
MW-26A	L5	Biennial	None	
MW-26B	L5	Semi-annual	None	
MW-27A	L5	None	None	
MW-27B	L5	None	None	
MW-29A	L3	None	None	
MW-29B	L3	Biennial	None	
MW-62AR	L6	Semi-annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-62B	L6	Semi-annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-62C	L6	Annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-63A	M6	Annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-63B	M6	Annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-65A	L6	Biennial	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-65B	L6	Semi-annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-65C	L6	Semi-annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping

TABLE 2

GROUNDWATER AND PUMPED GROUNDWATER SAMPLING SCHEDULE

PLUME Grouping Sample ID	Grid ID/ Sample Location	Sampling Frequency		Comments
		NPI VOCs	Cadmium	
MW-66A	L6	Semi-annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-66B	L6	Semi-annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping
MW-66C	L6	Semi-annual	None	Re-evaluate frequency if EW-1R and/or EW-2 resume pumping

NOTES:
Biennial = Sample collected in odd years only.
Lost = Well/piezometer has been lost. If the well/piezometer is found, then it will be sampled once for NPI VOCs and the results will be evaluated to determine if additional sampling is necessary.
NPI VOCs = l, l-DCA; l, l-DCE; PCE; l, l, l-TCA; and TCE.
Semi-annual = Semi-annual samples collected in second and fourth quarters (Q2/Q4); annual and biennial samples collected in Q2.

FOOTNOTES:
(1) Multi-level samples are collected from extraction wells that have been shut down, as requested by the WDNR.
(2) CAS-2R and MH-18 are located within 60 feet of each other. Consequently, we believe water quality is essentially the same at both locations. For this reason, we will sample MH-18 only, not both MH-18 and CAS-2R.
(3) MH-18 is sampled once a year for an expanded analyte list, per agreement with the WDNR. In odd years the list includes hardness (as CaCO3); cadmium, chromium, chromium+6, copper, lead, nickel, and zinc as total metals; PAHs; and pentachlorophenol. In even years, the list includes hardness (as CaCO3); cadmium, nickel, and zinc as total metals; and PAHs.
(4) Pumping from EW-1R and/or EW-2 will resume if an increasing trend in TCE or 1,1,1-TCA is observed in any of the MRDS monitoring wells (EW-1R, EW-2, MW-5A/B, MW-62A/B/C, MW-63A/B, MW-65A/B/C, and MW-66A/B/C).

APPENDIX A

PACE ANALYTICAL SOPs

Pace Analytical Services, LLC Green Bay, WI
1241 Bellevue Street Suite 9
Green Bay, WI 54302
Phone: 920 469-2436
Fax: 920 469-8827

STANDARD OPERATING PROCEDURE

Chromium, Hexavalent-Colorimetric

Reference Method: SM 3500 Cr-B-2009, Editorial Revision 2011

SOP NUMBER:	S-GB-I-045-REV.07
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-I-045-REV.06

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 10/24/16

Kate Verbeten, Laboratory Quality Manager — Date: 10/10/16

Chad Rusch, Department Manager — Date: 10/11/2016

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

This is **COPY#** ____ Distributed on _____ by _____ and is ____ **CONTROLLED**

Table of Contents

1. Purpose/Identification of Method

1.1 This procedure is used to determine the concentration of chromium (VI) in water as delineated in Standard Methods 3500-Cr-B-09.

2. Summary of Method

2.1 Dissolved hexavalent chromium is determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced.

2.2 The reaction is very sensitive: the absorbency index per gram atom of chromium is about 40,000 at 540nm. Addition of excess diphenylcarbazide yields the red-violet product, and its absorbance is measured at 540 nm.

3. Scope and Application

3.1 **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method or non-analytical process.

3.2 **Parameters:** This method measures chromium (VI) in waters at concentration from 20 to 600 µg/L. Additionally by client request, Trivalent Chromium can be determined by subtracting the Hexavalent Chromium result from the Total Chromium result.

4. Applicable Matrices

4.1 Drinking, ground, and surface waters

4.2 Domestic and industrial wastes

5. Limits of Detection and Quantitation

5.1 Current LOD and LOQ can be found in the Laboratory Information Management System (LIMS) - EpicPro.

5.2 Level of Detection (LOD): The LOD is determined by the 40CFR Part 136B MDL study. Once the 40CFR Part 136B MDL is determined it may be elevated if deemed unrealistic as demonstrated using method blank evaluations.

5.3 Level of Quantitation (LOQ): The LOQ is at least 3 times the LOD. A realistic LOD is typically near the lowest non-zero calibration point and higher than typical blank measurements.

6. Interferences

6.1 The chromium reaction with diphenylcarbazide is usually free from interferences.

6.2 A positive bias is observed in the presence of interfering amounts of substances such as hexavalent molybdenum, vanadium, and mercury salts. These salts will react to form color with the reagent but the intensities are much lower than that of chromium at the specified pH. Concentrations of Mo or Hg as high as 200 mg/L can be tolerated. Vanadium interferes strongly but concentrations up to 10 times that of chromium will not have a significant contribution.

6.3 Iron concentrations greater than 1mg/L can also produce a yellow color when reagents are added.

7. Sample Collection, Preservation and Handling

7.1 The lab provides appropriate bottle ware, including preservative, for requested testing. Where applicable, the bottle ware is demonstrated to be fee of target analytes. When bottle ware not originating from the lab is used, the data may be qualified with either one or both of the following data qualifiers:

7.1.1 Sample field preservation does not meet EPA or method recommendations for this analysis.

7.1.2 Sample container did not meet EPA or method requirements.

7.2 Samples are collected in clean glass or plastic containers.

7.3 The maximum holding time is 24 hours when refrigerated at ≤6°C.

7.4 Dissolved Samples are filtered prior to analysis.

8. Definitions

8.1 Definitions can be found in Section 10 of the most recent version of the Pace Analytical Services, LLC. Quality Manual.

9. Equipment and Supplies

9.1 Top loading Balance with 4 decimal places, OHAUS AP 110S or equivalent

9.2 Spectrophotometer, Hach DR2000 or equivalent, for use at 540 nM with light path of 1 cm or longer

9.3 25 mL graduated cylinder, Fisherbrand or equivalent

9.4 Adjustable pipetters – various sizes

9.5 Sample cells, Hach Cat# 13537-02 or equivalent

9.6 50 mL, 100 mL, and 1000 mL volumetric flasks, Pyrex or equivalent

9.7 Latex gloves

9.8 Finntip 5mL tips

9.9 Eppendorf 1000 µL Pipette tips

9.10 Eyedropper

9.11 Parafilm®

10. Reagents and Standards

10.1 Purchased Standards and Reagents

Standard	Alias	Purchased From	Catalog Number	Concentration /Purity	Expiration	Storage
Water	Nanopure®	In House	NA	≥18 mega ohms	Generated for use	Ambient
Potassium Dichromate (Primary)	Primary source standard	Fisher	P188-100	99.9%	manufacturer's not to exceed 5 years	Ambient
Potassium Dichromate (Secondary)	Secondary source standard	MP Biomedicals	194874	99.9%	manufacturer's not to exceed 5 years	Ambient
H_2SO_4	Concentrated Sulfuric Acid	Fisher	A298-212	Concentrated 93%-98%	manufacturer's not to exceed 2 years	Ambient
Color Reagent pillows	ChromaVer®3	Hach	12066-69	NA	manufacturer's	Ambient

10.2 Neat standards are dried at 105°C for minimum four hours and allowed to cool in a desiccator prior to being weighed out.

10.3 Working Standards and Reagents

Standard	Alias		Amount Used	Final Volume (W/Diluent)	Diluent	Final Conc.	Expiration	Storage
0.2N H2SO4	0.2N H2SO4	Concentrated Sulfuric Acid	5.52mL	1L	Water	0.2N	1 year not to exceed manufacturer's	Ambient
Primary Standard Solution	HEXCR-STK	Potassium Dichromate (Primary)	0.2121g	1L	Water	75.0 mg/L	1 year not to exceed manufacturer's	Ambient
Secondary Standard Solution	HEXCR-SPK	Potassium Dichromate (Secondary)	0.2121g	1L	Water	75.0 mg/L	1 year not to exceed manufacturer's	Ambient
Calibration Std 0	Cal 0	HEXCR-STK	0.00 mL	50 mL	Water	0.00 mg/L	Prepared Daily	NA
Calibration Std 1	Cal 1 and CRDL	HEXCR-STK	0.0267 mL	100 mL	Water	0.020 mg/L	Prepared Daily	NA
Calibration Std 2	Cal 2	HEXCR-STK	0.0666 mL	100 mL	Water	0.050 mg/L	Prepared Daily	NA
Calibration Std 3	Cal 3	HEXCR-STK	0.10 mL	50 mL	Water	0.150 mg/L	Prepared Daily	NA
Calibration Std 4	Cal 4	HEXCR-STK	0.20 mL	50 mL	Water	0.300 mg/L	Prepared Daily	NA
Calibration Std 5	Cal 5	HEXCR-STK	0.30 mL	50 mL	Water	0.450 mg/L	Prepared Daily	NA
Calibration Std 6	Cal 6	HEXCR-STK	0.40 mL	50 mL	Water	0.600 mg/L	Prepared Daily	NA
CCV	CCV	HEXCR-STK	0.10 mL	25 mL	Water	0.30 mg/L	Prepared Daily	NA
ICV	ICV	HEXCR-SPK	0.10 mL	25 mL	Water	0.30 mg/L	Prepared Daily	NA
MB	MB	NA	0.00 mL	25 mL	Water	0.0 mg/L	Prepared Daily	NA
LCS/LCSD	LCS/LCSD	HEXCR-SPK	0.10 mL	25 mL	Water	0.30 mg/L	Prepared Daily	NA
MS/MSD	MS/MSD	HEXCR-SPK	0.10 mL	25 mL	Sample	0.30 mg/L	Prepared Daily	NA

11. Calibration and Standardization

11.1 Create a Q-Batch in the LIMS.

11.2 Log into the Electronic Logbook and open the 3500/7196 Cr6 | Aq/Solid Hexavalent Chromium Analytical template. Pull the Q-Batch into the template.

11.3 Prepare a calibration curve using a minimum of five standards and a blank: see standards section 10. Pour standards into 25 mL cuvettes. All standards are prepared at the same time.

11.4 Turn on Spectrophotometer as per instrument manual and set to 540 nm. Let the instrument warm up at least 20 minutes.

11.5 Zero the spec on the Level 0 standard.

11.6 Wipe the outside of each cell with tissue paper to remove any fingerprints. Place ICB into the spectrophotometer and zero the instrument. Then, place the standard cells into the spectrophotometer and record standard absorbances at 540 nm into the excel spreadsheet. This should be done in order to account for coloration in the un-reacted sample.

11.7 With an eyedropper, add concentrated H_2SO_4 dropwise until a pH of 1.5 to 2.5 standard pH units is reached. One drop is typically added. Cover with Parafilm® and mix well. Repeat with each standard.

11.8 Add contents of color reagent powder pillow (ChromaVer®3) to standard, cover with Parafilm® and mix. Let stand 20 minutes. Repeat with each standard.

11.9 Wipe the outside of each cell with tissue paper to remove any fingerprints. Place ICB into the spectrophotometer and zero the instrument. Then, place the standard cells into the spectrophotometer and record standard absorbance at 540 nm into the excel spreadsheet. Repeat with each standard.

11.10 Enter the absorbance into the Electronic Logbook template.

11.11 A linear regression analysis of the absorbance values against the corresponding concentrations must yield a correlation coefficient of >0.995. The y-intercept must be less than the Pace Reporting Limit.

11.12 A new calibration curve should be prepared yearly at minimum or whenever the continuing calibration standard does not pass control criteria.

11.13 ICV, ICB, and CRDL standards, as made per section 9, are analyzed and record as in section 12 to validate the calibration.

12. Procedure

12.1 Batch the samples and QC in the LIMS.

12.2 Pull samples from Wet Chemistry cooler and allow them to reach room temperature.

12.3 Login and open the 3500/7196 Cr6 | Aq/Solid Hexavalent Chromium Analytical template. Pull in the sample batch and Q-Batch to populate the template.

12.4 Measure and pour 25 mL of sample into sample cells.

12.5 Create QC samples ICV, ICB, MB, LCS, MS, MSD, CCV, and CCB. Create CRDL standards if needed.

12.6 Wipe the outside of each cell with tissue paper to remove any fingerprints. Place ICB into the spectrophotometer and zero the instrument. Then, place the sample cells into the spectrophotometer and record sample and QC absorbances at 540 nm into the excel spreadsheet. This should be done in order to account *for* coloration in the un-reacted sample.

12.7 With an eyedropper, add 1 drop of concentrated H_2SO_4 to each sample including QC samples. Determine the pH of the adjusted sample using a pH meter and record on the benchsheet. Sample pH should fall between 1.5 and 2.5 standard pH units.

12.8 Add contents of color reagent powder pillow (ChromaVer®3) to each sample including QC samples and wait 20 minutes. Cover with Parafilm® and mix well.

12.9 Wipe the outside of each cell with tissue paper to remove any fingerprints. Place ICB into the spectrophotometer and zero the instrument. Then, place the sample cells into the spectrophotometer and record sample and QC absorbances at 540 nm into the Electronic Logbook template.

12.10 The Electronic Logbook template will subtract the sample absorbance from the reacted sample absorbance and calculate the sample results in µg/L Cr^{+6}. These results can then be posted to the LIMS in mg/L.

13. Quality Control

13.1 **Reporting Limit Verification Standard (CRDL)** – A standard prepared near the concentration of the LOQ. It is analyzed after the calibration and then monthly with acceptance criteria of standard recovery between 60-140% of true value. If outside the limits, reanalyze once. If still outside the limits, recalibrate.

13.2 **Initial Calibration Verification (ICV)**

13.2.1 The ICV must be analyzed immediately after calibration.

13.2.2 Concentration must be within ± 10% of the true value. When measurements are outside the control limits, the analysis must be terminated, the problem corrected, and the calibration re-verified.

13.2.3 The lot number of the potassium dichromate used to make the ICV must be different from that of the calibration curve standards.

13.3 C**ontinuing Calibration Verification (CCV)**

13.3.1 The CCV is analyzed after every 10 samples.

13.3.2 Concentration must be within ± 10% of the true value. When measurements are outside the control limits, the analysis must be terminated, the problem corrected, and the calibration re-verified. If the reset CCV fails recalibrate and reanalyze all samples back to the last acceptable CCV.

13.3.3 The lot number of the potassium dichromate used to make the CCV must be different from that of the ICV.

13.4 **Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)**

13.4.1 The ICB must be analyzed after the ICV. The CCB must be analyzed after the CCV.

13.4.2 The absolute value must be < LOQ. When measurements are above the LOQ, terminate analysis, correct the problem, verify the calibration, and reanalyze all analytical samples analyzed since the last compliant calibration blank.

13.4.2.1 Samples with concentrations greater than 10 times the absolute blank measurement may be reported unqualified.

13.4.2.2 Samples that have no detections may be reported unqualified if the blank measurement demonstrates a high bias.

13.5 **Method Blank (MB)**

13.5.1 The MB is laboratory grade water analyzed exactly like a sample. The MB is used to verify that interferences caused by contaminants in the solvents, reagents, glassware, etc. are known and minimized.

13.5.2 A MB must be analyzed with each batch of samples or every 20 samples, whichever is more frequent.

13.5.3 Acceptance Criteria: The MB is evaluated for both positive and negative bias and must have an absolute value less than the LOQ. For samples reporting down to the LOD, the MB measurements are evaluated to the LOD. In these cases qualify applicable samples for MB measurements from $\geq$LOD to $\leq$LOQ.

13.5.4 If the MB is greater than the LOQ, perform the following:

13.5.4.1 Check for errors in calculations. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.5.4.2 If there is sufficient sample available and hold time remaining, re-prepare the MB and all associated. If the MB is less than the LOQ in this analysis, accept the second set of data. If the MB is still outside the RL after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant MB.

13.5.4.3 If sufficient sample volume is not available, report the sample data with a qualifier flag on each of the samples associated with the non-compliant MB. Contact the project manager regarding the occurrence.

13.5.5 MB data qualifying

13.5.5.1 In the absence of project specific requirements, samples with concentrations greater than 10 times the absolute blank measurement may be reported unqualified.

13.5.5.2 In the absence of project specific requirements, samples that have no detections may be reported unqualified if the blank measurement demonstrates a positive bias.

13.5.5.3 In the absence of project specific requirements, samples that have no detections must be qualified if the blank measurement demonstrates a negative bias.

13.5.5.4 For samples that need qualification resulting from MB measurements that are positive, apply a B data qualifier to the analyte. B = "*Analyte was detected in the associated method blank.*"

13.5.5.5 For samples that need qualification resulting from MB measurements that are negative, apply a hand entered qualifier with the measurement and the units. "*Analyte was measured in the associated method blank at a concentration of -#.# units.*"

13.6 **Laboratory Control Sample (LCS)**

13.6.1 The LCS is carried through all preparation procedures and is made from a standard from different from that of the calibration curve.

13.6.2 The LCS is performed at a frequency of 5%, or one per batch of up to 20 environmental samples.

13.6.3 A Laboratory Control Spike Duplicate (LCSD) must be analyzed if there is insufficient sample volume to perform a matrix spike/matrix spike duplicate or if the client requests one.

13.6.4 Acceptance Criteria: Spike recovery must be within ± 10% of the true value. The true value is 0.30 mg/L.

13.6.5 If the LCS is outside the control limits, perform the following:

13.6.5.1 Check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

13.6.5.2 If there is sufficient sample available and hold time remaining, re-prepare the LCS (and/or LCSD) and all associated samples. If the recovery is within the limits in the analysis, accept the second set of data. If the recovery is still outside the limits after re-analysis, contact the PM to determine the resolution. If the client does not require additional work, report the data, applying an appropriate flag to the samples associated with the non-compliant LCS.

13.6.5.3 If sufficient sample volume is not available, report the sample data with the appropriate qualifier on each of the samples associated with the non-compliant LCS (and/or LCSD). Contact the project manager regarding the occurrence.

13.6.6 When an LCSD is performed, the precision between the LCS and LCSD must be ≤ 20% RPD.

13.6.6.1 See DUP for precision calculation.

13.6.6.2 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

13.6.6.3 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with appropriate data qualifier.

13.7 **Matrix Spike (MS) and Matrix Spike Duplicate (MSD)**

13.7.1 One pair of MS/MSD is performed at a frequency of 10%, or per up to 10 environmental samples, whichever is more frequent.

13.7.2 The sample used for MS/MSD pair is either determined by the client or selected at random from client samples as sample volume allows. No field, filter, trip or equipment blanks can be used for MS/MSD.

13.7.3 The MS and MSD and are made from a standard from different from that of the calibration curve.

13.7.4 Both QC samples must be calculated for accuracy and precision.

13.7.5 Acceptance Criteria: Spike recovery must be within ± 10% of the true value. The true value is 0.30 mg/L.

13.7.6 If the MS/MSD is outside the control limits, perform the following:

13.7.6.1 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

13.7.6.2 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with appropriate data qualifier.

13.7.7 The precision between the MS and MSD must be ≤ 20% RPD.

13.7.7.1 See DUP for precision calculation.

13.7.7.2 When measurements are outside the control limits, check for errors in calculations, standards preparation and spiking. If an error or problem is found and can be corrected by amending the calculations and the results falls within the limits, accept the data and report without a qualifier flag.

13.7.7.3 If no calculation errors are found when measurements are outside the control limits, flag the parent sample with appropriate data qualifier.

13.8 **Duplicate sample (DUP)**

13.8.1 A DUP is an aliquot of a sample to be analyzed along with the original sample. The DUP analysis indicates the precision associated with the sample collection, preservation and storage, as well as, laboratory procedures. An MSD is normally performed instead of a Duplicate Sample.

13.8.2 Duplicate sample analysis at a minimum will be performed at a frequency of 5% if requested by the client.

13.8.3 Acceptance limits: The RPD must be within 0-20% between the original sample and the duplicate.

13.8.4 If the RPD is exceeded, then:

13.8.4.1 Check for errors in calculations and sample preparation. If an error or problem is found and can be corrected by amending the calculations and the result falls within the limits, accept the data and report without a qualifier flag.

13.8.4.2 If no errors are found in calculations report the parent sample with the appropriate data qualifier.

13.9 **Hold Time** - When preparation of a sample exceeds 24 hours past the time of collection, notify the project manager before proceeding. If a sample is run past 24 hours after collection, flag the result with appropriate data qualifier.

13.10 If a sample was diluted due to matrix effects and the result is a non-detect, the result must be qualified with appropriate data qualifier.

14. Data Analysis and Calculations

14.1 LCS Percent Recovery is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{LCS concentration}}{\text{LCS known concentration}} \times 100$$

14.2 MS/MSD percent recovery is calculated as follows:

$$\% \text{ Recovery: } \frac{(SSR - SR)}{SA} \times 100$$

Where: SSR = spiked sample result, mg/L
SR =sample result, mg/L
SA = spike amount, mg/L

14.3 The relative percent difference (RPD) is calculated as:

$$\textbf{RPD} = \frac{|S - D|}{(S + D)/2} * 100$$

Where: **S** = sample value, mg/L
D = duplicate value, mg/L

14.4 Trivalent Chromium: Enter results onto Trivalent Chromium Bench sheet found in Attachment II. Calculation is performed as follows:

Trivalent Chromium = Total Chromium – Hexavalent Chromium

15. Data Assessment and Acceptance Criteria for Quality Control Measures

Table B: Data Assessment and Acceptance Criteria

Analytical Method ⇨ Calibration Measure ⇩	**SM3500Cr-B** **Frequency**	**Acceptance Criteria**
Laboratory Control Spike and Laboratory Control Spike Duplicate	• One LCS per batch of samples, up to 20 environmental samples, whichever is more frequent. • A LCSD is required if MS/MSD is not performed or if requested by the client.	• Project Specific or • Recovery of 90 –110% with 20% RPD
Matrix Spike / Matrix Spike Duplicate (MS/MSD)	• One pair per batch of samples, up to 10 environmental samples, whichever is more frequent.	• Project Specific or • Recovery of 90 –110% with 20% RPD
Method Blank	• One per batch of samples, up to 20 environmental samples, whichever is more frequent.	• Project Specific or • Less than the RL (LOWEST STANDARD IN CURVE)
Initial Calibration	• Analyzed daily before samples • Minimum 5 standards plus a blank	• Correlation coefficient must be 0.995 or greater
Initial Calibration Verification (ICV)	• Analyzed after calibration at.	• Recovery of 90 – 110%
Initial Calibration Blank (ICB)	• Analyzed after ICV pair but before samples.	• Project specific or • Less than LOQ
CRDL	• Analyzed after Initial Calibration. • Analyzed monthly thereafter at a minimum.	• 60-140%
Continuing Calibration Verification (CCV)	• Analyzed after every 10 samples.	• Project specific or • Recovery of 90 – 110%
Continuing Calibration Blank (CCB)	• After each CCV pair but before samples.	• Project specific or • Less than LOQ

16. Corrective Actions for Out-of-Control Data

Table C: CORRECTIVE ACTION

Analytical Method Acceptance Criteria⇨ Data Assessment Measure ⇩	**Method Citation: SM3500Cr-B** **If these conditions are not achieved ⇒**
Method Blank	• 1
Accuracy & Precision Matrix Spike Samples	• 2
Accuracy & Precision Laboratory Control Spikes	• 3
Initial Calibration	• 4
Initial / Continuing Calibration Verification	• 5
Initial / Continuing Calibration Blank	• 6
Holding Time Compliance	• 7
CRDL	• 8

1. If not <LOQ, verify by second analysis. If second analysis confirms contamination for target analyte at or greater than the LOQ, re-digest sample batch and batch QC provided sufficient sample volume remains. If insufficient sample volume remains, consult with project manager and client on how to proceed. For MB detections greater than or equal to the LOD, but less than the LOQ; qualify applicable sample results. For negative measurements more negative than the LOD, applicable data is given the following data qualifier: "Analyte was measured in the associated method blank at a concentration of -#.# units."
   * For positive MB failures, samples that are non-detection need not be qualified. In addition, samples that are greater than 10 times the MB detection need not be qualified.
   * For negative MB failures samples that are greater than 10 times the MB detection need not be qualified.

2. If the parent, MS, or MSD is greater than the reportable linear dynamic range, dilute and reanalyze the parent, MS, and MSD. If the concentration of the spike is less than 25% of the concentration of the parent the MS and MSD recoveries are not evaluated. Any failures resulting from this are qualified appropriately. If the concentration of the spike is greater than 25% of the concentration of the parent, appropriately qualify the parent sample if either the MS and/or MSD fail accuracy. If the MS and MSD fail precision control limits flag the parent with the appropriate precision data qualifier.

3. Verify failure by second analysis. If second analysis confirms LCS (LCSD) failure, re-digest sample batch and batch QC provided sufficient sample volume remains. If insufficient sample volume remains, consult with project manager and client on how to proceed.

4. If correlation coefficient is less than 0.995 perform maintenance and recalibrate.

5. If ICV/CCV is outside the control limits reanalyze the ICV/CCV to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.

6. If ICB/CCB is outside the control limits reanalyze the ICB/CCB to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. Samples that bracket the out of control standards must be reanalyzed.

7. Notify Project Manager by submitting a LabTrack Ticket and flag with the appropriate data qualifier.

8. If CRDL is outside the control limits reanalyze the CRDL to verify the instrument is out of control. If the 2nd analysis is outside control limits, perform maintenance and recalibrate. All applicable samples must be reanalyzed.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1 See Table C: Corrective Action and Attachment I: Flow Chart

18. Method Performance

18.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

18.2 The analyst must read and understand this procedure with written documentation maintained in his/her training file.

18.3 An initial demonstration of capability (IDOC) must be performed per the most recent version of S-ALL-Q-020, *Orientation and Training Procedure*s (most current revision or replacement). A continuing demonstration of capability (CDOC) must be performed annually. A record of the DOCs will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

18.4 At a minimum, the 40CFR part 136 appendix b study must be performed every year, per the most recent version of S-GB-Q-020, *Determination of the LOD and LOQ* (most current revision or replacement). Additional studies may be performed to achieve a realistic LOD and LOQ. This is to be done for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

18.5 A linear dynamic range study must be conducted at least once. The study is conducted for each element by analyzing increasing concentrations (at least 3 levels) until the results generated exceed ±10% difference from the true value. The highest concentration within the 10% criteria is the maximum of the linear range for that element. Once the linear dynamic range study determination is performed, keep the data, and then quarterly at a minimum verify with a single high point. Pace Analytical Services, LLC – Green Bay Laboratory will not use any data over the highest calibration standard used. All samples will be diluted and reanalyzed that are over the calibration range.

18.6 Periodic performance evaluation (PE) samples are analyzed per the most recent version of S-GB-Q-021 *PE/PT Program* (most current revision or replacement), to demonstrate continuing competence. All results are stored in the QA office. These are performed twice a year per matrix.

19. Method Modifications

19.1 Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.

19.2 All major modification to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.

19.3 Procedures identified as “Best Practices” by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories.

19.4 Calibration Curve and Sample Preparation: Reagent powder pillow (ChromaVer®3) is used in place of the diphenylcarbizide solution to develop color for the calibration curve and samples.

19.5 If a client fails to provide sufficient volume for the method required Matrix Spike/Matrix Spike Duplicate (MS/MSD), the laboratory will analyze a Laboratory Control Spike Duplicate to demonstrate precision. The analytical batch will be qualified with the "M5" data qualifier.

19.6 SM 3500-Cr B Editorial revisions, 2011 says to use 0.2*N* H_2SO_4 to adjust the sample pH to 2.0±0.5 pH units. Pace WI uses concentrated H_2SO_4.

20. Instrument/Equipment Maintenance

20.1 See HACH DR2000 Spectrophotometer operator's manual for information.

21. Troubleshooting

21.1 See HACH DR2000 Spectrophotometer operator's manual for information.

22. Safety

22.1 All samples, standards, and reagents should be treated as hazardous. Safety glasses, gloves, and lab coats are to be worn. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by a safe technique. Special care should be taken when handling the high concentration acids and oxidizing reagents used for sample digestion.

22.2 The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of any chemical. A reference file of Safety Data Sheets (SDS) and a formal safety plan are made available to all personnel involved in chemical analysis and should be consulted prior to handling samples and standards.

23. Waste Management

23.1 Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult the current version of S-GB-W-001, *Waste Handling and Management*.

24. Pollution Prevention

24.1 Pollution prevention encompasses any technique or procedure that reduces or eliminates the quantity or toxicity of waste at the point of generation.

24.2 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

24.3 The laboratory Chemical Hygiene Plan/Health and Safety Plan contains additional information on pollution prevention.

25. References

25.1 Standard Methods for the Examination of Water and Wastewater, SM 3500-Cr-B-09, Editorial Revision 2011.

26. Tables, Diagrams, Flowcharts, Appendices, Addenda etc.

26.1 Attachment 1: Trivalent Chromium Benchsheet

26.2 Flowchart

27. Revisions

Revision Number	Reason for Change	Date
S-GB-I-045-Rev.06	Updated Method reference to SM 3500Cr-B-09, Editorial Rev 2011 Sections 3, 14 and Attachment II: Updated to include Trivalent Chromium information. Section 9.4: Added solution of 0.2N H2SO4. Sections 11.5 and 12.4: Replaced the use of concentrated sulfuric acid with 0.2N H2SO4. Table A and B: Incorporated into Body of the Text and removed from Attachments. Updated Attachment. I: Hexchrome Benchsheet	21Jan2014
S-GB-I-045-Rev.07	Throughout document: Updated Pace Analytical Services, Inc to Pace Analytical Services, LLC Updated numbering throughout SOP Section 3.2: Removed LOD/LOQ. Section 5: Updated definitions of LOD and LOQ. Section 7: Added language when qualifiers are added if non-Pace containers are used. Section 9: Changed to Equipment and Supplies. Section 10: Changed to Standards and Reagents. Added Tables 10.1 and 10.3. Section 11: Updated with electronic preplog information. Section 12.7: Changed to adding 1 drop concentrated H2SO4. Section 13: Updated QC sample language. Section 18: Added requirement of LDR. Section 19.6: Added. Removed Attachment I: moved to electronic prep log Updated Trivalent Chromium Bench sheet	10Oct2016

Attachment I Trivalent Chromium Benchsheet

Pace Analytical™

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Trivalent Chromium

Method: 3500Cr+B/6010/6020/200.7/200.8
Calculation Date: __________
Matrix: Water
Units: ug/L

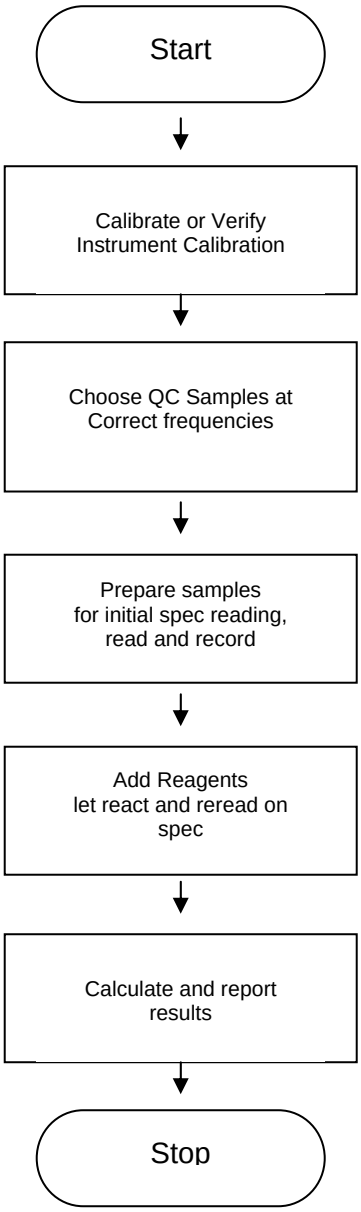
Analyst: __________
HBN: __________
WET Batch: __________
Secondary Review (Initial/Date): __________

Lab #	Chromium		Hexavalent Chromium		**Trivalent Chromium**	Sample	Sample
	Analysis Date	Result	Analysis Date	Result	**Final Result[1, 2]**	MDL	EQL
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		
					0.00		

1 - No QC for Trivalen Chromium was run. Results were derived from Total Chromium and Hexavalent Chromium results which both had the proper QC.
2 - Results less than the MDL are not factored into the calculations for the Trivalent Chromium results.

F-GB-I-179-Rev,04 (10Oct2016)
Pace Analytical - Green Bay Laboratory

Attachment II: Flowchart



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STANDARD OPERATING PROCEDURE

Determination of Metals by Inductively Coupled Plasma (ICP) Spectroscopy

Reference Methods: SW-846 6010B, SW-846 6010C and EPA 200.7; SM 2340B-2011

SOP NUMBER:	S-GB-M-005-REV.08
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-M-005-REV.07

APPROVAL

Nils Melberg, Laboratory General Manager — Date: 06/21/17

Kate Verbeten, Laboratory Quality Manager — Date: 6/21/17

Chad Rusch, Department Manager — Date: 06/21/2017

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date
Signature	Title	Date
Signature	Title	Date

This is **COPY#** ____ Distributed on _____ by _____ and is ____ **CONTROLLED**

Table of Contents

1. Purpose/Identification of Method

1.1 This Standard Operating Procedure (SOP) documents the procedures used by PASI – Wisconsin to determine the concentration of specific metals in environmental water, wipe, paint chips, sludges, soils, and solid samples. The laboratory utilizes the ICP (Inductively Coupled Plasma – Optical Emission Spectrometer) and bases these documented procedures on those listed in EPA SW-846 Method 6010B, 6010C and EPA 200.7. Sample preparation procedures are based on SW-846 Methods 3010A, 3050B, and EPA-200.7.

2. Summary of Method

2.1 Samples are digested, excluding filtered groundwater for 6010B/6010C analysis, by heating with appropriate acids and oxidizing agents to solubilize the target elements. Portions of the digestates (or filtered, acidified groundwater samples) are pumped into a nebulizer to produce an aerosol. The aerosol is aspirated into the torch of an Inductively Coupled argon Plasma Optical Emission Spectrometer (ICP-OES) where it is evaporated and decomposed into atoms and ions. The plasma energy causes the target atoms to become excited and, during relaxation, emit characteristic light in the visible and/or ultraviolet emissions. Each element in the sample emits photons at a discrete wavelength(s), which are specific to that element. The light emissions are separated into wavelength and order by passing through a prism and onto an Echelle grating. The signal is then read and quantified by a Charge Injection Device (CID). The intensities of the wavelengths are proportional to the quantity of the target elements that is determined through a comparison to a known concentration (a calibration curve). The signals received from the CID are digitized and relayed to the instrument computer as an analytical signal.

2.2 Background correction is required to compensate for spectral interferences. Background is measured adjacent to analyte lines at a wavelength selected to be free of spectral interference and which reflects 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 correction would actually degrade the analytical result.

3. Scope and Application

3.1 This procedure may be used to determine concentrations of trace metals in water, wipe, paint chip, sludge, soil, and solid samples. A list of applicable elements, wavelengths used, and on instrument concentrations used to validate LOQs are shown in Table 3.1.

Table 3.1 – Elements, wavelengths, and on instrument CRDL RL concentrations used to validate LOQs.

Element		Wavelength (nm)	RL (µg/L)
Ag	Silver	328.0	10.0
Al	Aluminum	396.1	500
As	Arsenic	189.0	20.0
B	Boron	208.9	40
Ba	Barium	455.4	5.0
Be	Beryllium	313.0	4.0
Ca	Calcium	317.9	500
Cd	Cadmium	228.8	5.0
Co	Cobalt	228.6	5.0
Cr	Chromium	267.7	10.0
Cu	Copper	324.7	10.0
Fe	Iron	259.9	100
K	Potassium	766.4	1,000
Mg	Magnesium	279.0	1,000
Mn	Manganese	257.6	5.0
Mo	Molybdenum	202.0	10
Na	Sodium	589.5	500
Ni	Nickel	231.6	10.0
Pb	Lead	220.3	12.0
Sb	Antimony	206.8	20.0
Se	Selenium	196.0	20.0
Sn	Tin	189.9	25
Sr	Strontium	407.7	5.0
Ti	Titanium	334.9	5.0
Tl	Thallium	190.8	40.0
V	Vanadium	292.4	10.0
Zn	Zinc	206.2	40.0

3.2 This procedure is restricted to use by, or under the supervision of, analysts experienced in the digestion of samples for metals analysis and analysis of digestates by ICP. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.3 This method cannot be substituted for other similar published methods where permit or regulatory compliance is required.

3.4 Current Method Detection Limits can be found in current LIMS or can be provided by the Quality Department.

4. Applicable Matrices

4.1 This SOP is applicable to un-digested dissolved aqueous samples analyzed by 6010B or 6010C.

4.2 This SOP is applicable to digested aqueous (dissolved, total, waste) samples analyzed by 6010B, 6010C, and 200.7.

4.3 This SOP is applicable to digested solid/soil/sludge samples analyzed by 6010B, 6010C, and 200.7.

4.4 This SOP is applicable to digested paint chip samples analyzed by 6010B, 6010C, and 200.7.

4.5 This SOP is applicable to digested wipe samples analyzed by 6010B, 6010C, and 200.7.

5. Limits of Detection and Quantitation

5.1 All current MDLs and LOQs are listed in the LIMS and are available by request from the Quality Manager. The lowest concentrations that element recoveries are verified at with a standard can be found in Table 3.1.

6. Interferences

6.1 Spectral Interferences – Overlap of emission lines from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena and stray light can contribute to spectral interferences. These interferences can typically be minimized by careful selection of quantitation wavelengths, background correction, and inter-element corrections.

6.2 Physical Interferences –Changes in sample viscosity, surface tension, or other effects associated with sample transport and nebulization can produce significant inaccuracies, especially in samples containing high concentrations of dissolved solids and acids. Dissolved solids may build up on the nebulizer tip, altering the sample flow rate and causing instrument drift. These effects can be minimized by sample dilution, use of a specially designed high-solids nebulizer, or an argon humidifier. Use of internal standards helps in recognizing sample introduction issues.

6.3 Chemical Interferences – Molecular compound formation, ionization effects, and solute vaporization effects are typically not significant with ICP determinations. If observed, they can be minimized by careful selection of plasma and spectrometer operating parameters.

6.4 Memory Interferences – Sample deposition on the nebulizer tubing, spray chamber, and plasma torch can cause apparent sample carryover. Memory interferences can be minimized by flushing the system with rinse blanks between samples. If memory interference is suspected for a sample, the sample must be re-analyzed after a sufficient rinse period.

6.5 High Salt Concentrations – High salt concentrations in sample digestates can cause signal suppression and confuse interference tests. Use of internal standards helps in recognizing signal suppression.

7. Sample Collection, Preservation, Shipment and Storage

7.1 The lab provides appropriate bottle ware, including preservative, for requested testing. Where applicable, the bottle ware is demonstrated to be fee of target analytes. When bottle ware not originating from the lab is used, the data may be qualified with either one or both of the following data qualifiers:

7.1.1 Sample field preservation does not meet EPA or method recommendations for this analysis.

7.1.2 Sample container did not meet EPA or method requirements.

7.2 Collection, Preservation, Storage and Hold Times

Sample type	Collection per sample	Preservation	Storage	Hold time
Soil/ Solid/ Wipe/Paint Chip/Sludge	Pre-cleaned plastic or glass containers. Refer to Pace SOP S-GB-Q-025, *Sample Homogenization and Sub-Sampling* (current revision or replacement), for obtaining representative aliquots.	No Preservation	Refrigerated at ≤6°C	Up to 6 months
Total Metals – Aqueous	Pre-cleaned plastic containers with HNO_3	Nitric Acid (HNO_3) to pH<2, preserved at time of collection	Room Temperature	Up to 6 months
Dissolved Metals – Aqueous(1)	Pre-cleaned plastic containers – Filter sample at time of collection through a 0.45µm membrane filter.	Nitric Acid (HNO_3) to pH<2, filtered then preserved at time of collection.	Room Temperature	Up to 6 months
TCLP/SPLP/ASTM(2)	Pre-cleaned plastic containers.	Filtered then preserved at time of digestion. -Refrigerate at ≤6°C until preservation. -Nitric Acid (HNO_3) to pH<2	Refrigerate at ≤6°C	From Field Collection to Leach Extraction: 180 Days. From Leach Extraction to Determinative Analysis: 180 Days. (Total Elapsed Time: 360 Days).

(1) If filtration cannot be performed in the field, the sample must be taken in a pre-cleaned, unpreserved plastic container and transported to the lab as soon as possible. The sample must be filtered and then preserved to a pH <2. The sample must sit for **24 hours** prior to preparation, to ensure that the sample does not have a buffering effect that raises the pH to above <2. All lab filtered samples are qualified for improper field preservation.

(2) TCLP Extracts are not required to sit for 24 hours prior to digestion after the addition of nitric acid.

7.3 Preservative Check - The pH of samples must be verified to be <2 and documented in the Sample Receiving or Metals pH logbook prior to taking an aliquot for analysis. If a sample has a pH>2, additional preservative must be added to bring the sample to pH<2. Acid volume shall not to exceed 2% of the container capacity. Once adjusted, the sample must be allowed to sit for 24 hours prior to preparation. If the sample is not able to maintain a preservation of a pH of<2, then it must be qualified as such.

8. Definitions

8.1 Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions. In addition to those listed in the QAM, the following are additional terms found in this SOP.

8.2 Instrumental Detection Limit (IDL) – The concentration equivalent to a signal, due to the analyte, which is equal to the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with ten consecutive measurements per day at the same wavelength.

8.3 Instrument Check Standard – A multi-element standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. This is the same as the Continuing Calibration Verification Standard (CCV) referred to in the calibration section of this SOP.

8.4 Spectral Interference Check Solution (SIC) – A solution of selected analytes of higher concentrations used to evaluate the procedural routine for correcting known inter-element spectral interferences. This is also known as the Inter-element Correction Solution (ICSA).

8.5 Linear Detection Range – Defined as the upper limit of quantitation for an analyte. The LDR is determined as the upper range limit of an observed signal that deviates no more than 10% from the level extrapolated from the lower standards.

8.6 Interference Check Sample - (ICSAB) – A solution containing both interfering and analyte elements of known concentration that can be used to verify background and inter-element correction factors.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1 Instrumentation

Equipment	Vendor	Model / Version	Description / Comments
iCAP System	Thermo Scientific	ICAP 6500	Serial Number: 20073913
Autosampler	ESI	SC4 DX	X4DXS-HS-TSP-16-111004
Data System	iTEVA	2.0.039	
Recirculator	Neslab	ThermoFlex900	Serial Number: 107271037

9.2 General Supplies

Item	Vendor (or equivalent)	Catalog # (or equivalent)	Description
Argon – high purity grade	PraxAir	-----	Bulk
Autosampler Vials	Fisher Scientific	14-375-150	15 mL Polypropylene Test Tubes
Autosampler Pump Tubing	Analytical West	PT-2130PS-F PT-2200SAS PT-2080PS-F	black/black 0.76mm ID – Carrier 1.30mm ID – Waste orange/green 0.38mm ID – Internal Standard
Digestion Vials	SCP Science	010-500-263	Pre-cleaned polypropylene 50-mL screw cap vials.
Mechanical Pipettes and Tips	Eppendorf	Various	Or equivalent
Filter paper	Whatman	541 Filter Paper	
pH Strips	Fisherbrand	13-640-500	pH range 0 to 3
Y Connectors	Hewlett-Packard	G1820-65106	
Duo Torch / Duo Ceramic Cone	Thermo Fisher Scientific	8423-120-51241 / 84223-120-51261	
Spray Chamber/Spray Chamber adapter	Thermo Fisher Scientific	8423-120-51411 / 8423-120-51251	
SC-FAST Probe	ESI	SC-5037-3995-150	7” Teflon/Carbon Probe 1.0mmID
SC-FAST Waste Line	ESI	SC-0323-0002-215	Waste Line
SC-FAST Valve	ESI	SC-0599-1024	F7 Valve Head
	ESI	ES-2501-PPF2	
	ESI	ES-2501-PPMZ	
Peri-Pump	ESI		Fluoropolymer union, barbed
Nebulizer Line	ESI	SC-0317-0250-30	
Nuts and Ferrules	ESI	SC-0599-0116-K	For high flow 1/16” tubing
Nuts and Ferrules	ESI	SC-0599-0108-W	For high flow 1/8” tubing
Vacuum Line	ESI	SC-0321-32-215	For SC-FAST high flow valve
Sample Loop	ESI	SC-0318-15	1.5mL sample loop
Nebulizer	ESI	ES-2040	Micro Flow PFA-St nebulizer

9.3 Glassware

Glassware	Description
Volumetric Flasks	Class A
Graduated Cylinders	Class A

10. Reagents and Standards

10.1 Reagents

Reagent	Concentration/ Description	Requirements/ Vendor/ Item #	Expiration Date
Nano-pure Water	ASTM Type II, or equivalent (18mOhm or higher resistivity)	Nano-pure Water	NA
Nitric Acid (HNO_3)	Trace metals grade, Fisher Insta-analyzed, or equivalent	J.T Baker Cat #9598-34 or equivalent	Manufacturer's recommended expiration date or 2 years from receipt/made date, whichever is sooner
Hydrochloric Acid (HCl)	Trace metals grade, Fisher Insta-analyzed, or equivalent	Fisher Cat # A508 or equivalent	
Hydrogen Peroxide (H_2O_2)	30% certified reagent grade; trace metals grade if available. Stabilized solutions come with Sodium added.	Fisher Cat # H325-4 or equivalent	
Acidified Reagent Water	5mL Nitric Acid and 5mL Hydrochloric Acid per 100mL Nano-pure water	NA	

10.2 Standards

10.2.1 Standards are used in the calibration of the instrument through the calibration verification, sample analysis, and continuing calibration verification.

10.2.2 Primary standards are the calibration standards and those that are made from the same source as the calibration standards.

10.2.3 Secondary standards are made from a source that is from a different vendor/manufacturer than the calibration source.

10.2.4 Whenever possible, standards are prepared from commercially available multi-component stock solutions. Single stock standards may also be utilized.

10.3 Standards, Reagents, and Spike Solutions are logged as follows:

10.3.1 Stock standards have a copy of their certificate of analysis (COA) scanned and saved on the network. The standard is logged into the LIMS (Epic Pro) and referenced to the scanned COA. Please see the SOP G-ALL-IT-004 (most current revision or equivalent) for more detailed instructions.

10.3.2 Reagents are logged in the same manner.

10.4 Standard Definitions

Standard 6010B/6010C	Standard 200.7	Description	Comments
Initial Calibration Standard(s)	Initial Calibration Standard(s)	Standard(s) prepared from single and/or multi-element standard(s) at appropriate acid concentrations.	Calibration standards can be made and used for 6 months unless a standard used to make them expires earlier.
Initial Calibration Verification Standard (ICV)	Quality Control Sample (QCS) & 1st IPC	Standard prepared near the midpoint of the calibration range and is used to verify the accuracy of the calibration and instrument performance.	Must be prepared from a source independent of CCV and Calibration Solutions.
Continuing Calibration Verification Standard (CCV)	Instrument Performance Check Solution (IPC)	Standards prepared from single and/or multi-element standards at appropriate acid concentrations. Solutions containing all analyte elements are prepared at a concentration near the mid-point of the calibration range. This standard verifies the accuracy of the calibration curve.	May be prepared from the same source as the calibrations standards
Reporting Limit Verification Standard (RLVS)	NA	A standard prepared and analyzed at the RL (near the LOQ) to demonstrate the detection capability and verify the LOQ.	NELAC requirement, a client specific requirement for certain QAPPs
Inter-element correction solution (ICSA)	Spectral Interference Solution (SIC)	A solution prepared with high concentrations of interfering elements (Al, Ca, Fe, Mg...). This is run daily at a minimum to verify the inter-element correction factors.	Al, Ca, Fe, Mg
Inter-element correction solution (ICSAB)	NA	A solution prepared with high concentrations of interfering elements and low level concentrations of the other target elements. This is analyzed daily and immediately following the ICSA solution.	Not a 6010B, 6010C, or 200.7 requirement, but may be required on a client specific basis.
Internal Standard (IS)	Internal Standard (IS)	A solution added to all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard solution contains a non-target element (yttrium (Y)) at a concentration yielding an appropriate final concentration in the sample.	Y at 5ppm with Li. Added in-line to all samples and standards.
Single Element Standards	Single Element Standards	Stock standards purchased from venders containing one element. Used for checking IECs and may be used for checking linear ranges.	Must be 99.99% or more pure.
Spiking Standard	Spiking Standard	This solution contains all target analytes and should not be prepared from the same standards as the calibration standards.	Prepared from a source independent of CCV and Calibration Solutions.
Method Blank (MB)	Laboratory Reagent Blank (LRB)	This blank must contain all the reagents, in the same volumes as used for samples and must be carried through the complete processing of samples with the samples.	
Laboratory Control Sample (LCS)	Laboratory Fortified Blank (LFB)	Lab water spiked with the reagents of interest at a known concentration. It must contain all the reagents, in the same volumes as used for samples and must be carried through the complete processing of samples with the samples.	Spiked from a source independent of CCV and Calibration Solutions.
Matrix Spike (MS), Matrix Spike Duplicate (MSD)	Laboratory Fortified Sample Matrix (LFM)	Aliquots of environmental sample spiked with known concentrations of target analytes.	Spiked from a source independent of CCV and Calibration Solutions.

10.5 Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date.	▪ Manufacturer's recommended storage conditions ▪ When standard is opened, record all information in the standard logbook.
Intermediate and Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ Should be prepared as needed or at least every 6 months. The intermediate or working standard can not exceed the expiration date recommended by the manufacturer for each component used.	▪ Store at room temperature

10.6 Calibration Working Standard – Dilutions and Concentrations

Pace Custom Standard (Stock Standard)	Element Components	Stock Concentration	Stock Volume Used	Acid Used	Final Total Volume	Final Concentration in Standard
Metals STK1 = Spex #1 (XFSMN-26-250A)	As	100 mg/L	2 mL	10 mL HNO_3 / 10 mL HCl	200 mL	1.0 mg/L
	Ba	100 mg/L				1.0 mg/L
	Be	100 mg/L				1.0 mg/L
	Cd	100 mg/L				1.0 mg/L
	Co	100 mg/L				1.0 mg/L
	Cr	100 mg/L				1.0 mg/L
	Cu	100 mg/L				1.0 mg/L
	Mn	100 mg/L				1.0 mg/L
	Ni	100 mg/L				1.0 mg/L
	Pb	100 mg/L				1.0 mg/L
	Se	100 mg/L				1.0 mg/L
	Sr	100 mg/L				1.0 mg/L
	Tl	100 mg/L				1.0 mg/L
	V	100 mg/L				1.0 mg/L
	Zn	100 mg/L				1.0 mg/L
Metals STK2 = Spex #2 (XFSMN-27-250A)	B	100 mg/L	4 mL			2.0 mg/L
	Mo	100 mg/L				2.0 mg/L
	Sb	100 mg/L				2.0 mg/L
	Sn	100 mg/L				2.0 mg/L
	Ti	100 mg/L				2.0 mg/L
	Ag	50 mg/L				1.0 mg/L
Metals STK3 = Spex #3 (XFSMN-28-250A)	Al	1,000 mg/L	10 mL			50 mg/L
	Ca	1,000 mg/L				50 mg/L
	Fe	1,000 mg/L				50 mg/L
	K	1,000 mg/L				50 mg/L
	Mg	1,000 mg/L				50 mg/L
	Na	1,000 mg/L				50 mg/L

10.7 CCV Working Standard – Dilutions and Concentrations

Pace Custom Standard (Stock Standard)	Element Components	Stock Concentration	Stock Volume Used	Acid Used	Final Total Volume	Final Concentration in Standard
Metals STK1 = Spex #1 (XFSMN-26-250A)	As	100 mg/L	5.0 mL	50 mL HNO_3/ 50 mL HCl	1000 mL	0.5 mg/L
	Ba	100 mg/L				0.5 mg/L
	Be	100 mg/L				0.5 mg/L
	Cd	100 mg/L				0.5 mg/L
	Co	100 mg/L				0.5 mg/L
	Cr	100 mg/L				0.5 mg/L
	Cu	100 mg/L				0.5 mg/L
	Mn	100 mg/L				0.5 mg/L
	Ni	100 mg/L				0.5 mg/L
	Pb	100 mg/L				0.5 mg/L
	Se	100 mg/L				0.5 mg/L
	Sr	100 mg/L				0.5 mg/L
	Tl	100 mg/L				0.5 mg/L
	V	100 mg/L				0.5 mg/L
	Zn	100 mg/L				0.5 mg/L
Metals STK2 = Spex #2 (XFSMN-27-250A)	B	100 mg/L	10.0 mL			1.0 mg/L
	Mo	100 mg/L				1.0 mg/L
	Sb	100 mg/L				1.0 mg/L
	Sn	100 mg/L				1.0 mg/L
	Ti	100 mg/L				1.0 mg/L
	Ag	50 mg/L				0.5 mg/L
Metals STK3 = Spex #3 (XFSMN-28-250A)	Al	1,000 mg/L	25.0 mL			25 mg/L
	Ca	1,000 mg/L				25 mg/L
	Fe	1,000 mg/L				25 mg/L
	K	1,000 mg/L				25 mg/L
	Mg	1,000 mg/L				25 mg/L
	Na	1,000 mg/L				25 mg/L

10.8 ICV (Second Source) Working Standard – Dilutions and Concentrations

Pace Custom Standard (Stock Standard)	Element Components	Stock Concentration	Stock Volume Used	Acid Used	Final Total Volume	Final Concentration in Standard
Metals SPK1 = IV #1 (PA-STD-1B)	As	200 mg/L	0.5 mL	10 mL HNO_3/ 10 mL HCl	200 mL	0.5 mg/L
	Ba	200 mg/L				0.5 mg/L
	Be	200 mg/L				0.5 mg/L
	Cd	200 mg/L				0.5 mg/L
	Co	200 mg/L				0.5 mg/L
	Cr	200 mg/L				0.5 mg/L
	Cu	200 mg/L				0.5 mg/L
	Mn	200 mg/L				0.5 mg/L
	Ni	200 mg/L				0.5 mg/L
	Pb	200 mg/L				0.5 mg/L
	Se	200 mg/L				0.5 mg/L
	Sr	200 mg/L				0.5 mg/L
	Tl	200 mg/L				0.5 mg/L
	V	200 mg/L				0.5 mg/L
	Zn	200 mg/L				0.5 mg/L
Metals SPK2 = IV #2 (PA-STD-2B)	B	200 mg/L	1.0 mL			1.0 mg/L
	Mo	200 mg/L				1.0 mg/L
	Sb	200 mg/L				1.0 mg/L
	Sn	200 mg/L				1.0 mg/L
	Ti	200 mg/L				1.0 mg/L
	Ag	100 mg/L				0.5 mg/L
Metals SPK3 = IV #3 (PA-STD-3B)	Al	2,000 mg/L	2.5 mL			25 mg/L
	Ca	2,000 mg/L				25 mg/L
	Fe	2,000 mg/L				25 mg/L
	K	2,000 mg/L				25 mg/L
	Mg	2,000 mg/L				25 mg/L
	Na	2,000 mg/L				25 mg/L

10.9 Spiking Standard 6000-SPK (for LCS and MS/MSD) – Dilutions and Concentrations

Pace Custom Standard (Stock Standard)	Element Components	Stock Concentration	Stock Volume Used	Acid Used	Final Total Volume	Final Concentration in Standard	Spike Concentration
Metals SPK1 = IV #1 (PA-STD-1B)	As	200 mg/L	25 mL	12 mL HNO_3	200 mL	25 mg/L	500 ug/L
	Ba	200 mg/L				25 mg/L	500 ug/L
	Be	200 mg/L				25 mg/L	500 ug/L
	Cd	200 mg/L				25 mg/L	500 ug/L
	Co	200 mg/L				25 mg/L	500 ug/L
	Cr	200 mg/L				25 mg/L	500 ug/L
	Cu	200 mg/L				25 mg/L	500 ug/L
	Mn	200 mg/L				25 mg/L	500 ug/L
	Ni	200 mg/L				25 mg/L	500 ug/L
	Pb	200 mg/L				25 mg/L	500 ug/L
	Se	200 mg/L				25 mg/L	500 ug/L
	Sr	200 mg/L				25 mg/L	500 ug/L
	Tl	200 mg/L				25 mg/L	500 ug/L
	V	200 mg/L				25 mg/L	500 ug/L
	Zn	200 mg/L				25 mg/L	500 ug/L
Metals SPK2 = IV #2 (PA-STD-2B)	B	200 mg/L	25 mL			25 mg/L	500 ug/L
	Mo	200 mg/L				25 mg/L	500 ug/L
	Sb	200 mg/L				25 mg/L	500 ug/L
	Sn	200 mg/L				25 mg/L	500 ug/L
	Ti	200 mg/L				25 mg/L	500 ug/L
	Ag	100 mg/L				12.5 mg/L	250 ug/L
Metals SPK3 = IV #3 (PA-STD-3B)	Al	2,000 mg/L	25 mL			250 mg/L	5,000 ug/L
	Ca	2,000 mg/L				250 mg/L	5,000 ug/L
	Fe	2,000 mg/L				250 mg/L	5,000 ug/L
	K	2,000 mg/L				250 mg/L	5,000 ug/L
	Mg	2,000 mg/L				250 mg/L	5,000 ug/L
	Na	2,000 mg/L				250 mg/L	5,000 ug/L

10.10 Low Level Check Standard (6010CRDL-INT) Intermediate

Pace Custom Standard (Stock Standard)	Element Components	Stock Concentration	Stock Volume Used*	Acid Used	Final Total Volume	Final Concentration in Standard
6010CRDL-STK = 4400-161007AM01	Ag	10 mg/L	10 mL	5 mL HNO_3 / 5 mL HCl	100 mL	1,000 ug/L
	Al	500 mg/L				50,000 ug/L
	As	20 mg/L				2,000 ug/L
	B	40 mg/L				4,000 ug/L
	Ba	5 mg/L				500 ug/L
	Be	4 mg/L				400 ug/L
	Ca	500 mg/L				50,000 ug/L
	Cd	5 mg/L				500 ug/L
	Co	5 mg/L				500 ug/L
	Cr	10 mg/L				1,000 ug/L
	Cu	10 mg/L				1,000 ug/L
	Fe	100 mg/L				10,000 ug/L
	K	1,000 mg/L				1000,000 ug/L
	Mg	1,000 mg/L				1000,000 ug/L
	Mn	5 mg/L				500 ug/L
	Mo	10 mg/L				1,000 ug/L
	Na	500 mg/L				50,000 ug/L
	Ni	10 mg/L				1,000 ug/L
	Pb	12 mg/L				1,200 ug/L
	Sb	20 mg/L				2,000 ug/L
	Se	20 mg/L				2,000 ug/L
	Sn	25 mg/L				2,500 ug/L
	Sr	5 mg/L				500 ug/L
	Ti	5 mg/L				500 ug/L
	Tl	40 mg/L				4,000 ug/L
	V	10 mg/L				1,00 ug/L
	Zn	40 mg/L				4,000 ug/L

10.11 Low Level Check Standard (ICP-CRDL) Working Solution – Dilutions and Conc.

Low Level Check Standard Intermediate	Element Components	Stock Concentration	Stock Volume Used*	Acid Used	Final Total Volume	Final CRDL Concentration
6010CRDL-INT = CRDL Intermediate	Ag	1,000 ug/L	2 mL	10 mL HNO_3 / 10 mL HCl	200 mL	10 ug/L
	Al	50,000 ug/L				500 ug/L
	As	2,000 ug/L				20 ug/L
	B	4,000 ug/L				40 ug/L
	Ba	500 ug/L				5 ug/L
	Be	400 ug/L				4 ug/L
	Ca	50,000 ug/L				500 ug/L
	Cd	500 ug/L				5 ug/L
	Co	500 ug/L				5 ug/L
	Cr	1,000 ug/L				10 ug/L
	Cu	1,000 ug/L				10 ug/L
	Fe	10,000 ug/L				100 ug/L
	K	100,000 ug/L				1,000 ug/L
	Mg	100,000 ug/L				1,000 ug/L
	Mn	500 ug/L				5 ug/L
	Mo	1,000 ug/L				10 ug/L
	Na	50,000 ug/L				500 ug/L
	Ni	1,000 ug/L				10 ug/L
	Pb	1,200 ug/L				12 ug/L
	Sb	2,000 ug/L				20 ug/L
	Se	2,000 ug/L				20 ug/L
	Sn	2,500 ug/L				25 ug/L
	Sr	500 ug/L				5 ug/L
	Ti	500 ug/L				5 ug/L
	Tl	4,000 ug/L				40 ug/L
	V	1,000 ug/L				10 ug/L
	Zn	4,000 ug/L				40 ug/L

10.12 Inter-element Correction Solution (ICP-ICSA) Working Solution – Dilutions and Conc.

Pace Standard #	Vendor	Stock Catalog Number	Stock Volume Used	Final Total Volume	Acid Used	Element Components	Final Concentration in Standard	Stock Concentration
Single Element Al	Ultra Scientific	ICP-113	5 mL	200 mL	10 mL HNO_3 / 10 mL HCl	Al	250 mg/L	10,000 mg/L
Single Element Ca	Ultra Scientific	ICP-120	10 mL			Ca	500 mg/L	10,000 mg/L
Single Element Mg	Ultra Scientific	ICP-112	10 mL			Mg	500 mg/L	10,000 mg/L
Single Element Fe	Ultra Scientific	ICP-126	4 mL			Fe	200 mg/L	10,000 mg/L

10.13 Inter-element Correction Solution (ICP-ICSAB) Working Solution – Dilutions and Conc.

Pace Standard #	Vendor	Stock Catalog Number	Stock Volume Used	Final Total Volume	Acid Used	Element Components	Final Concentration in Standard	Stock Concentration
Single Element Al	Ultra Scientific	ICP-113	4.5 mL	200 mL	10 mL HNO_3 / 10 mL HCl	Al	225 mg/L	10,000 mg/L
Single Element Ca	Ultra Scientific	ICP-120	9.5 mL			Ca	475 mg/L	10,000 mg/L
Single Element Mg	Ultra Scientific	ICP-112	9.5 mL			Mg	475 mg/L	10,000 mg/L
Single Element Fe	Ultra Scientific	ICP-126	3.5 mL			Fe	175 mg/L	10,000 mg/L
Metals SPK1	Inorganic Ventures	PA-STD-1B	0.5 mL			As	0.5 mg/L	200 mg/L
						Ba	0.5 mg/L	200 mg/L
						Be	0.5 mg/L	200 mg/L
						Cd	0.5 mg/L	200 mg/L
						Co	0.5 mg/L	200 mg/L
						Cr	0.5 mg/L	200 mg/L
						Cu	0.5 mg/L	200 mg/L
						Mn	0.5 mg/L	200 mg/L
						Ni	0.5 mg/L	200 mg/L
						Pb	0.5 mg/L	200 mg/L
						Se	0.5 mg/L	200 mg/L
						Sr	0.5 mg/L	200 mg/L
						Tl	0.5 mg/L	200 mg/L
						V	0.5 mg/L	200 mg/L
						Zn	0.5 mg/L	200 mg/L
Metals SPK1	Inorganic Ventures	PA-STD-2B	1.0 mL			B	1.0 mg/L	200 mg/L
						Mo	1.0 mg/L	200 mg/L
						Sb	1.0 mg/L	200 mg/L
						Sn	1.0 mg/L	200 mg/L
						Ti	1.0 mg/L	200 mg/L
						Ag	0.5 mg/L	100 mg/L
Metals SPK3	Inorganic Ventures	PA-STD-3B	2.5 mL			Al	25 mg/L	2,000 mg/L
						Ca	25 mg/L	2,000 mg/L
						Fe	25 mg/L	2,000 mg/L
						K	25 mg/L	2,000 mg/L
						Mg	25 mg/L	2,000 mg/L
						Na	25 mg/L	2,000 mg/L
Single Element Ni	Ultra Scientific	ICP-028	0.1 mL			Ni	0.5 mg/L	1,000 mg/L

10.14 Internal Standard Solution – Dilutions and Concentrations

Pace Standard #	Stock Catalog Number	Stock Volume Used	Final Total Volume	Acid Used	Element Components	Final Concentration in Standard	Stock Concentration
ICP-IS	ICP-139 (ULTRA SCIENTIFIC)	0.5 mL	1000 mL	50 mL HNO_3 / 50 mL HCl	Yttrium	5 mg/L	10,000 mg/L
	CGLI10 (Inorganic Ventures)	100 mL			Lithium	1,000 mg/L	10,000 mg/L

11. Calibration and Standardization

11.1 Rinse Time – Both the SW846 6010 methods and EPA 200.7 specify a minimum of a 1.0 min rinse time. The sample loads for about 14 seconds. For the remainder of the 2.0 min plus timeframe the system is being rinsed.

11.2 Nebulizer Flow Rate – This is to be done at set-up, or after an operating condition change. A 10,000ug/L Yttrium standard will yield a "bullet" emission about 10mm beyond load coil. Adjust the nebulizer flow rate to modify the "bullet" location.

11.3 Solution Uptake Rate – This is a visual check of a bubble in the loop to verify that the sample is reaching the nebulizer in sufficient time for analysis. This should be done when the timing is suspected to be off. Adjust the pump settings if adjustments are needed.

11.4 Profile - The iCAP 6500 ICP will automatically check a carbon reference line against ambient air conditions each time the plasma is ignited to maintain wavelength accuracy.

11.5 Daily Initial Calibration

11.5.1 Allow the instrument 30 minutes to warm up after igniting the torch.

11.5.2 The ICP must be calibrated each time it is set up for analysis or every 24 hours according to the manufacturer's instructions.

11.5.3 Calibration requires analysis of a Calibration Blank and at least one level of calibration solution. The ICP software will create a calibration curve using linear regression.

11.5.4 Calibration standards can be made and used for 6 months unless a standard used to make them expires earlier. It would then expire on that date. Instrument standardization date and time must be recorded in the raw data.

11.6 During the determination, the software uses the ratio of analyte and internal standard intensities to adjust the final concentration values. Ratios are based on the intensities in the sample vs. the calibration blank intensities.

11.7 Calibration Verification- Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. This is accomplished by analyzing and passing the following QC points: ICV, ICB, CRDL, and ICSA standards. Additional verification is required periodically throughout sample analysis as dictated by the method being cited. These QC points may include CCVs, CCBs, ICSAs, ICSABs, and/or CRDLs.

12. Procedure

12.1 ICP System Preparation

12.1.1 Preventative Maintenance

Inspect the sample introduction system including the nebulizer, torch, injector tube and up-take tubing for salt deposits, dirt and debris that could restrict solution flow and affect instrument performance. Document all maintenance in ICP maintenance logbook.

12.1.2 Operating Parameters

Set up and configure the ICP according to manufacturer's operating instructions using operating parameters shown in the following table.

Table 11.3.1 - Operating Parameter for ICP Systems

Operating Parameter	ICAP 6500 20073913
Argon Flow	80 L/min
Nebulizer Flow	0.70 L/min
RF Output	1175 W
Pump Speed	30 rpm
Aux Gas Flow	0.5 L/min
Coolant Gas Flow	15 l/min

12.1.3 Calibrate ICP according to Section 11.

12.1.4 Batch Sequence - If using an auto-sampler, enter an auto-sampler sequence into the ICP data system per manufacturer's instructions. Calibration blanks, standards, initial checks, and inter-element correction standards shall be run before analysis of environmental samples. All samples, including calibration, checks, and other standards, can also be run manually.

12.1.5 For dissolved batches prepare the batch QC as follows:

12.1.5.1 MB – Add 10 mL of acidified reagent water to an auto-sampler tube.

12.1.5.2 LCS/LCSD – Add 0.20 mL of 6000-SPK to 10 mL of acidified reagent water in an auto-sampler tube.

12.1.5.3 MS/MSD – Add 0.20 mL of 6000-SPK to 10 mL of parent sample in an auto-sampler tube.

12.1.6 Load auto-sampler tray according to the vial position on the sequence table.

12.1.7 Analyze all standards, quality control samples, and environmental samples.

Table 12.0 – 6010C Example analytical sequence after calibration of a blank and a standard.

Auto-sampler Position	Sample Description	Auto-sampler Position	Sample Description
1	ICV	27	Sample 15
2	ICB	28	Sample 16
3	CRDL	29	CCV
4	ICSA *	30	CCB
5	CCV	31	Sample 17
6	CCB	32	Sample 18
7	MB1	33	Sample 19
8	LCS1	34	Sample 20
9	Sample 1	35	MB2
10	Sample 1 Matrix Spike	36	LCS2
11	Sample 1 Matrix Spike Duplicate	37	Sample 21
12	Sample 2	38	Sample 22
13	Sample 3	39	Sample 22 Matrix Spike
14	Sample 4	40	Sample 22 Matrix Spike Duplicate
15	Sample 5	41	CCV
16	Sample 6	42	CCB
17	CCV	43	Sample 25
18	CCB	44	Sample 26
19	Sample 7	45	Sample 27
20	Sample 8	46	Sample 28
21	Sample 9	47	Sample 28 Matrix Spike
22	Sample 10	48	Sample 28 Matrix Spike Duplicate
23	Sample 11	49	CCV
24	Sample 12	50	CCB
25	Sample 13	51	CRDL
26	Sample 14		

* ICSAB will follow the ICSA if needed/requested by client.

12.2 Data Reduction

12.2.1 **Quantitative Analysis –** The instrument produces results in µg/L. If the initial sample aliquot and final digestate volumes are the same, the ICP data system will calculate the concentration of each element directly. If the initial and final volumes are different, the actual values are posted into the LIMS system and calculations are performed in the LIMS.

12.2.2 Analysts should be aware situations where possible carryover can occur. This can be seen when highly concentrated samples are analyzed followed by analysis of detections with decreasing concentration. Every element reacts differently and sample matrix can play a role as well. Should carryover be suspected by the analyst, the affected sample(s) should be reanalyzed.

12.2.3 Samples with element concentrations that exceed 90% of the upper linear range must be diluted and re-analyzed if reporting that element and/or if that element interferes with another element that is being reported.

12.2.4 Any sample in which any element value is below the instrument detection limit or LOQ must be reported as less than the LOQ (or ND) for that specific element. Do not report data below the element LOQ concentration unless it is qualified as an "estimated" result with a "J".

12.2.5 LimsLink is used to transfer data from the instrument to the LIMS system.

13. Quality Control

There are three levels of quality control utilized in this SOP. They consist of Method QC, Instrument QC, and Prep/Batch QC.

13.1 Refer to the most current version of the Pace Quality Manual Appendix I Quality Control Calculations and SOP S-GB-Q-009 *Common Laboratory Calculations and Statistical Evaluation of Data* for equations and calculation details.

13.2 **Instrument QC**: Prior to the analysis of samples, and in some cases during the analysis run, the following quality control must be generated and/or within limits: Internal Standards, Interference Correction Solutions A and B (ICSA and ICSAB), Initial Calibration Verification (ICV), Continuing Calibration Verification (CCV), RLVS / CRDL standards, and Initial and Continuing Calibration Blanks (ICB and CCB).

13.2.1 **Internal Standards –** Yttrium is used as an internal standard. Yttrium is not calibrated for. Precision of the Yttrium reps are evaluated using < or = 5% RSD. Accuracy of the Yttrium average count levels are evaluated using 50-150% recovery as compared to the calibration blank. If either of these criteria is not meet, the sample or quality control standard must be rerun, possibly at a dilution. Criteria may be tighter to meet certain client or project specifications.

13.2.2 **Multiple Instrument Integration RSD** – The RSD is required to be evaluated between multiple instrument integrations. The RSD must be less than or equal to 20%, if the analyte concentration is greater than the RL. If the RSD is greater than 20%, the laboratory must reanalyze the sample.

13.2.3 The ICSA and ICSAB solution are used to verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run, prior to the analysis of any samples. By client request the ICSA and ICSAB may also be analyzed at the end of the analytical sequence. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. The control limits for the elements in the ICSAB solution that are in the linear range must be within 80 to 120% of the expected recovery. Non-spiked elements must have a result less than the LOQ unless there is a known contaminant. In this case the result minus the known contaminant must result in a concentration less than the LOQ. If an element of interest does not meet these criteria, then the problem must be corrected, the instrument recalibrated, and the run reanalyzed.

13.2.4 The ICV is analyzed to check the accuracy of the curve. It must be evaluated before any samples are analyzed. The ICV should be at or near (or lower than) the midpoint of the calibration curve, derived from a source independent of the calibration standards, and must recover within 90 to 110% of the expected

value for 6010B and 6010C. For 200.7 the ICV must recover within 95 to 105% of the expected value and have an RSD of <3%. If these limits are not met for an element of interest, the problem must be corrected, the instrument recalibrated, and the run reanalyzed. If the ICV fails high and the samples are non-detects, then they may be reported. Pace WI satisfies the 200.7 QCS and first Instrument Performance Check (IPC) criteria using the ICV.

13.2.5 Reporting Limit Verification Standard (RLVS/RL/CRDL): With every Initial Calibration, a standard corresponding to the Level of Quantitation (LOQ) must also be analyzed and meet established acceptance criteria. The concentrations in the CRDL are determined to be the reporting limit (RL). The RLVS is analyzed prior to any samples being analyzed. For 6010C and by client request it will also be analyzed at the end of the analytical sequence. Additional RLVSs may be analyzed throughout the analytical sequence at the analyst's discretion. The limits for the RLVS are +/- 40% of the true concentration for 6010B and 200.7. The limits for the RLVS are +/- 30% of the true concentration for 6010C. The analysis of this standard demonstrates the instruments ability to quantify down to the LOQ with known accuracy.

13.2.6 The CCV is analyzed to check for calibration drift. The CCV is run after every 10 samples and again at the end of samples. It must quantitate within 90 to 110% of the expected value. Any sample analyzed under out-of-control calibration must be reanalyzed, following the successful re-calibration of the instrument. If the CCV fails high and the samples are non-detects, then they may be reported. Pace WI satisfies the 200.7 Instrument Performance Check (IPC) criteria using the CCV, with the exception of the first IPC.

13.2.7 The ICB is analyzed to check the accuracy of the curve. The CCBs are analyzed to check for calibration drift. In the absence of project specific reporting limits, the results of the calibration blanks must be less than the LOQ. The ICB is run after the ICV and the CCBs are run after the CCVs. If the ICB or CCB fails high for an analyte and the samples are non-detects or are greater than 10x the blank value, then they may be reported.

13.3 **Batch Quality Control** - A batch will consist of 20 or fewer samples. Batch Quality Control will include a Method Blank (MB), Laboratory Control Spike (LCS), Matrix Spike (MS), Matrix Spike Duplicate (MSD). It may also include a Laboratory Control Spike Duplicate (LCSD), Post Spike (PS), a Serial Dilution (SDL), Duplicate (DUP), additional MS/MSDs, and/or Standard Reference Material (SRM).

13.3.1 The Method Blank is used to verify that interferences caused by contaminants in the solvents, reagents, glassware, etc. are known and minimized. The method blank is processed through all digestions, etc., which were performed on the samples in the batch. For a method blank to be acceptable, in the absence of project specific criteria, the concentration shall not be higher than the highest of the following: The LOQ, or ten percent of the regulatory limit of concern for that analyte, or ten percent of the measured concentration in a particular sample of interest. Each sample in the batch is assessed against the above criteria to determine if the sample results are acceptable. Any sample associated with an unacceptable blank is either flagged, re-prepped for analysis, or if re-prepping is not an alternative, the results are reported with the appropriate data qualifying codes. For negative instrument measurements >LOD and <LOQ qualify sample results that are non-detections and <10 times the measurement with "Analyte was measured in the associated method blank at a concentration of -#.# units." Make sure to enter the concentration and applicable sample units.

13.3.2 A laboratory control sample (LCS) consists of a control matrix, which has been spiked, with the analytes(s) of interest or compounds representative of those analytes. Laboratory Control Samples are analyzed at a minimum of 1 per batch of 20 or fewer samples or preparation method. Results of the LCS are expressed in terms of percent recovery, and are used to determine batch acceptance. Acceptance limits can be generated based on laboratory generated data and are not to exceed 80 to 120% of the expected recovery for 6010B and 6010C, or 85 to 115% for 200.7. If these limits are not met and the failure is confirmed by a single re-analysis, with the instrument in control, then the entire batch will be re-digested and re-analyzed. Data for high LCS failure can be reported if the analyte is non-detection.

13.3.3 An LCS Duplicate may be analyzed to evaluate laboratory precision. The LCSD must also meet the criteria for the LCS. The Relative Percent Difference (RPD) will be calculated between the LCS and LCSD. The RPD is calculated as outlined below:

The control limit for RPD is based on laboratory generated data and is not to exceed 20%. If outside this limit, verify with another analysis. If the RPD is still outside of criteria, the batch must be re-digested and analyzed provided sufficient sample volume. If there in not enough sample volume to re-digest, then the data must be qualified. Data generated with LCS samples that fall outside the established acceptance criteria are judged to be out-of-control. These data are considered suspect and the corresponding samples are reanalyzed or reported with qualifiers.

NOTE: In the event where adequate sample is not supplied by the client to perform a Matrix Spike/ Matrix Spike Duplicate, the LCS and duplicate can lend insight on the precision of the analysis.

13.3.4 Matrix spikes (MS and MSD) are performed to evaluate the effect of the sample matrix upon analytical methodology. A separate aliquot of sample is

spiked with the analyte of interest and analyzed with the sample. For 6010B and 6010C an MS and MSD are performed at a minimum frequency of 5% per batch. One pair in 20 samples, per matrix type, per sample preparation method and are performed more frequently where regulations require. For 200.7, an MS/MSD pair, are performed at a 10% frequency per batch. Matrix spike recoveries are evaluated against in-house control limits. The recovery must not exceed 75 to 125% of the expected recovery for 6010B or 6010C. The recovery must not exceed 70 to 130% of the expected recovery for 200.7. If outside this recovery, the parent is flagged with an appropriate data qualifier. If the recovery of an analyte is outside this range but the spike level in not at least 25% the background concentration in the parent sample, the data is flagged with an appropriate data qualifier. The RPD between the MS and MSD must be less than 20 %. If outside this limit, the parent is given an appropriate data qualifier. The parent sample for the MS/MSD is chosen at random unless specified by a client. Poor performance in a matrix spike generally indicates a problem with the sample composition, and not the laboratory analysis, and results are used to assist in data assessment. A matrix effect is indicated if the LCS data are within acceptance criteria but the matrix spike data exceed the acceptance criteria. Prior to calculating recovery, the parent sample concentration (results <Reporting MDL = 0) is subtracted from the spike aliquot concentrations.

13.3.5 The Post Spike (PS) can be run to verify matrix interferences. An analyte spike added to a portion of a prepared sample, or its dilution, must be recovered to within 80 to 120% (85 to 115% for 200.7) of the known value. If the spike is not recovered within the specified limits with the instrument in control, then the sample has a confirmed matrix effect. The sample is diluted and spiked until acceptable recoveries are achieved. A PS is run for 6010C batches, by client request, and for QC 3 or 4 data deliverable work orders.

13.3.6 The Serial Dilution (SDL) can be run to check for matrix interferences. If the analyte concentration is within the linear dynamic range (LDR) of the instrument and sufficiently high (minimally, a factor of at least 10 times greater than the lower limit of quantitation for the diluted sample, or 50 times the RLVS standard for the parent sample) an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If these limits are not met then an interference effect must be suspected and the data qualified with an SD flag. If the analytes of interest are greater than the LDR in the parent sample, the sample can be diluted and an SDL done off of the dilution.

13.3.7 A Duplicate (DUP) is run to verify precision either from within the lab or from sampling. Typically the MSD or LCSD serve as the precision control for a sample batch. These will have concentrations for target elements greater than the LOQ, where as a typical sample may not. Sample DUPs are analyzed when requested by the client or QAPP. For concentrations $\geq$ the LOQ two separate aliquots processed in the same batch must have an RPD $\leq$ 20%. Each aliquot must be $\geq$ LOQ. If they do not have an RPD within criteria and no errors are found, qualify the DUP and Parent with an R1 data qualifier.

13.3.8 An SRM can be digested and analyzed upon client request and lab pre-approval. It is a sample of known concentration chosen to resemble the matrix

being analyzed. An SRM is digested and analyzed with each batch of coarse/fine Pb samples.

14. Data Analysis and Calculations

14.1 The iTEVA software performs all calculations necessary to convert raw counts per second data into quantitative concentration results.

14.2 Relative Percent Difference (RPD)

$$RPD = \frac{|D_1 - D2|}{(D_1, + D_2,)/2} \times 100$$

Where:
RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate)

14.3 % Recovery = [Result –True Value] / True Value * 100

14.4 Aqueous Sample Calculation:

$$\frac{\text{Raw Data result (µg/L)} * DF * VF}{V_I} = \text{Final Result (µg/L)}$$

Where:
DF = Dilution Factor
V_F = Final Volume (L)
V_I = Initial Sample Volume (L)

14.5 Soil Sample Calculation:

$$\frac{\text{Raw Data result (µg/L)} * DF * V_F}{W_S \times \%S} = \text{Final Result (mg/kg dry weight)}$$

Where:
DF = Dilution Factor
V_F = Final Volume (L)
V_I = Initial Sample Volume (L)
W_S = Sample weight (grams)

%S = Percent solids/ 100
Example: For a sample that is 97.6% solid use 0.976

14.6 Wipe Sample Calculation:

$$\frac{\text{Raw data result (µg/L)} * VF * DF}{1 \text{ wipe}} = \text{Final Result (Total µg)}$$

Where:
DF = Dilution Factor
V_F = Final Volume (L)

14.7 Determination of Hardness by SM 2340B: The measure to precipitate soap was the original definition of Hardness. The main two ion species that are responsible for hardness are Calcium and Magnesium. Current Total Hardness is defined as the sum of Calcium (Ca) and Magnesium (Mg) concentration expressed as Calcium Carbonate ($CaCO_3$)

14.7.1 Hardness as $CaCO_3$ in mg/L = 2.497 * $[Ca_{\text{in mg/L}}]$ + 4.118 * $[Mg_{\text{in mg/L}}]$

14.8 IEC calculations - To set up Initial IEC, run single element standards with only background correction points in place. The standards are run at the linear range.

$$IEC = \frac{\text{Element result (µg/L)}}{\text{Interfering element result (µg/L)}}$$

Where the Element result (ug/L) is the apparent concentration.

This ratio is entered in the IEC table in the method file. Type the ratio under the k1 header in the appropriate row. Enter a negative before the ratio if it is a negative interference.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

Analytical Method Criteria⇨ Data Assessment Measure ⇩	6010B/6010C Frequency	6010B/6010C Acceptance Criteria	200.7 Frequency	200.7 Acceptance Criteria
MB	One per batch, not to exceed 20samples.	>LOD<LOQ - Qualify > LOQ – Re-digest w/ exceptions	One per batch, not to exceed 20samples.	>LOD<LOQ - Qualify > LOQ – Re-digest w/ exceptions
LCS/LCSD	One LCS per batch, not to exceed 20samples. LCSD performed by client request or if insufficient sample volume for MS/MSD.	±20% recovery of the true value. ≤20% RPD	One LCS per batch, not to exceed 20samples. LCSD performed by client request or if insufficient sample volume for MS/MSD.	±15% recovery of the true value. ≤20% RPD
MS/MSD	One pair per batch of 20 or fewer samples.	±25% recovery of the true value. ≤20% RPD	One pair per batch of 10 or fewer samples.	±30% recovery of the true value. ≤20% RPD
PS	6010B- By client request, once per batch of 20 or fewer samples. 6010C- Once per batch of 20 or fewer samples.	±20% recovery of the true value.	By client request.	±15% recovery of the true value.
SDL	6010B – By client request, once per batch of 20 or fewer samples. 6010C- Once per batch of 20 or fewer samples.	±10% RPD referenced to the parent.	By client request.	±10% RPD referenced to the parent.
DUP	By client request.	≤20% RPD	By client request.	≤20% RPD
SRM	One per batch of 20 or fewer samples. Coarse/Fine Pb analysis.	Reference only. Client specific acceptance criteria.	Possible if pre-approved from a client request.	
ICV	Once right after calibration, prior to any samples being analyzed.	±10% recovery of the true value.	Once right after calibration, prior to any samples being analyzed.	±5% recovery of the true value. RSD <3%.
ICB	Once right after ICV.	<RL	Once right after ICV.	<RL
ICSA	Prior to any samples, typically after the CRDL.	±20% recovery of the true value. <RL for analytes with no concentration.	Prior to any samples, typically after the CRDL.	±20% recovery of the true value. <RL for analytes with no concentration.
ICSAB	After the ICSA.	±20% recovery of the true value.	After the ICSA, by client request.	±20% recovery of the true value.
CRDL (RL Standard)	6010B - After the ICB. 6010C - After the ICB and bracketing samples.	6010B - ±40% recovery of the true value. 6010C - ±30% recovery of the true value.	Prior to samples being analyzed, after the ICB.	±40% recovery of the true value.
CCV	Bracket every 10 or fewer samples. After any samples.	±10% recovery of the true value.	Bracket every 10 or fewer samples. After any samples.	±10% recovery of the true value.
CCB	Right after CCVs.	<RL	Right after CCVs.	<RL

16. Corrective Actions for Out-of-Control Data

Analytical Method Criteria⇨ Data Assessment Measure ⇩	If acceptance criteria are not achieved ⇒
MB	• 1
LCS/LCSD	• 2
MS/MSD	• 3
PS	• 4
SDL	• 5
DUP	• 6
SRM	• 7
ICV	• 8
ICB	• 9
ICSA	• 10
ICSAB	• 11
CRDL	• 12
CCV	• 13
CCB	• 14

1. If not <LOQ, verify by second analysis. If second analysis confirms contamination for target analyte at or greater than the LOQ*, re-digest sample batch and batch QC provided sufficient sample volume remains. If insufficient sample volume remains, consult with project manager and client on how to proceed. For MB detections greater than or equal to the LOD but less than the LOQ qualify applicable sample results*.
   * For any positive MB failures, samples that are non-detection need not be qualified. In addition, samples that are greater than 10 times the MB detection need not be qualified and can be reported.

2. If LCS/LCSD fail criteria, verify by second analysis. If second analysis confirms LCS (LCSD) failure*, re-digest sample batch and batch QC provided sufficient sample volume remains. If insufficient sample volume remains, consult with project manager and client on how to proceed. * For any biased high LCS/LCSD failures, samples that are non-detection may be reported without qualification.

3. If the parent, MS, or MSD is greater than the reportable linear dynamic range, dilute and reanalyze the parent, MS, and MSD. If the concentration of the spike is less than 25% of the concentration of the parent the MS and MSD recoveries are not evaluated. Any failures resulting from this are qualified appropriately. If the concentration of the spike is greater than 25% of the concentration of the parent, appropriately qualify the parent sample if either the MS and/or MSD fail accuracy. If the MS and MSD fail precision control limits flag the parent with the appropriate precision data qualifier.
4. If the PDS is not recovered within the specified limits with the instrument in control, dilute the parent and re-spike the diluted sample until the PS recovers within acceptance criteria.

5. If the SDL limits are not met, then an interference effect must be suspected and the data qualified with an appropriate data qualifier. If the analytes of interest are greater than the LDR in the parent sample, the sample is diluted and an SDL done off of the dilution.

6. If the DUP fails precision control limits flag the parent with the appropriate precision data qualifier.

7. For Coarse/Fine Pb analysis only. The SRM is digested and analyzed only to demonstrate analyte recovery in a standard reference material.

8. If ICV fails, verify by second analysis. If second analysis confirms ICV failure, correct the issue and recalibrate the instrument. No data may be reported unless there is a passing ICV for that target analyte.

9. If ICB fails, verify by second analysis. If second analysis confirms ICB failure, correct the issue and recalibrate the instrument. No data may be reported unless there is a passing ICB for that target analyte, unless the failure is biased high and the sample is non-detection, or the sample concentration is greater than 10 times the detection in the ICB for that target analyte.

10. If ICSA fails, verify by second analysis. If second analysis confirms ICSA failure, the system is out of control. Correct the issue and recalibrate the instrument. No data may be reported unless there is a passing ICSA for that target analyte.

11. If ICSAB fails, verify by second analysis. If second analysis confirms ICSAB failure, the system is out of control. Correct the issue and recalibrate the instrument. No data may be reported unless there is a passing ICSAB for that target analyte.

12. If CRDL fails, verify by second analysis. If second analysis confirms CRDL failure, the system is out of control. . Correct the issue and recalibrate the instrument. No data may be reported unless there is a passing CRDL for that target analyte. * For any positive CRDL failures, samples that are non-detection may be reported without qualification. In addition, samples that have concentrations greater than the CCV may also be reported, provided the bracketing CCVs are within control.

13. If CCV fails, verify by second analysis. If second analysis confirms CCV failure, correct the issue and recalibrate the instrument. On unattended sequence, CCVs may fail and then pass later in the sequence. No data may be reported unless bracketed by passing CCVs for that target analyte, unless the CCV fails high and the sample is non-detection.

14. If CCB fails, verify by second analysis. If second analysis confirms CCB failure, correct the issue and recalibrate the instrument. On unattended sequence, CCBs may fail and then pass later in the sequence. No data may be reported unless bracketed by passing CCBs unless the failure is biased high and the sample is non-detection, or the sample concentration is greater than 10 times the detection in the CCB for that target analyte.

Note: Second analysis for verification must pass for all target elements to be completely valid. If Pb is the only target element that fails on the first analysis and passes on the second analysis, it is valid. However, if As passes on the first, but then fails on the verification, then that QC point is no longer within control for As.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

See section 16 Corrective Actions for Out-of-Control Data

18. Method Performance

18.1 **LOD/LOQ** - At a minimum, the 40CFR part 136 appendix b study must be performed every year, per the most recent version of S-GB-Q-020, *Determination of the LOD and LOQ* (most current revision or replacement). Additional studies may be performed to achieve a realistic LOD and LOQ. This is to be done for this method and whenever there is a major change in personnel or equipment. The results of these studies are retained in the quality assurance office.

18.2 **An initial demonstration of capability (IDOC)** – IDOCs must be performed per the most recent version of S-ALL-Q-020, *Orientation and Training Procedure*s (most current revision or replacement). A continuing demonstration of capability (CDOC) must be performed annually. A record of the DOCs will be maintained in his/her QA file with written authorization from the Laboratory Manager and Quality Manager.

18.3 **Linear Dynamic Range Study (LDR)** - It is a Pace best practice to perform this linear dynamic range study determination once, keep the data. The study is conducted for each element by analyzing increasing concentrations (at least 3 levels) until the results generated exceed ±10% difference from the true value. The highest concentration within the 10% criteria is the maximum of the linear range for that element. Subsequent studies are performed with a single high point to verify the LDR.The linear dynamic range verification study is performed in conjunction with the IEC studies at a minimum of every 6 months.

18.4 **Instrument Detection Limits (IDLs)** in µg/L are estimated 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 ten consecutive measurements per day. 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 normally performed between the analysis of separate samples). IDLs must be determined at least quarterly.

18.5 **Inter-Element Corrections (IECs)** - IECs go through a full evaluation a minimum of once every six months. This is done simultaneously with the Linear Dynamic Range Studies. Adjustments may also be made if ICSA analysis demonstrates the need for an IEC to be updated sooner. IECs are calculated from observed interferences witnessed from the analysis of single element standard analyzed at the LDR. The observed element interference result is divided by the on instrument reading of the interfering element. This factor is entered into the IEC tab on the element list of the method in the instrument software.

18.6 **Lower limit of quantitation check sample (LLQC)** - The LLQC samples should be analyzed after establishing the LOQs, and on an as needed basis to demonstrate the desired the detection capability. The LLQC sample is carried through the entire preparation and analytical procedure. Acceptance criteria are ±30% of the true value.

18.7 **Periodic performance evaluation (PE)** - PE samples are analyzed per the most recent version of S-GB-Q-021 *PE/PT Program* (most current revision or replacement), to demonstrate continuing competence. All results are stored in the QA office. These are performed twice a year per matrix.

18.8 **Quality Control Sample (QCS from 200.7)** - This standard is from a source different than that of the calibration standards. It is made using the same acids and concentrations as the calibration standards. This standard is used to validate the calibration standards and the calibration. For 200.7 analysis Pace WI combines the QCS and first IPC criteria and meets them with the ICV. The acceptance criteria is +/-5% of the true value with the RSD on four replicates being <3%.

19. Method Modifications

19.1 The digestion procedures are based on, but differ somewhat from 200.7, 3010A, and 3050B. Pace Wisconsin has conducted temperature, time, and side by side studies to validate the digestions utilized. Pace Wisconsin digestions are typically more aggressive with higher acid concentrations than the methods listed.

19.2 Method modifications for EPA method 6010B, 6010C, and 200.7 are as follows:

19.3 Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.

19.4 All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.

19.5 Procedures identified as “Best Practices” by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories

19.6 When there is insufficient volume provided by the client for the method specified matrix spike/matrix spike duplicate (MS/MSD), a laboratory control spike duplicate will be analyzed to demonstrate precision criteria. Laboratory batches will be qualified with the appropriate “M5” data qualifier. When performing this analysis on paint chip samples, a MS/MSD will not be completed on the samples due to high levels of elements present in the native sample.

20. Instrument/Equipment Maintenance

20.1 See Thermo ICAP 6500 Duo operator’s manual for information.

21. Troubleshooting

21.1 See Thermo ICAP 6500 Duo operator’s manual for information.

21.2 Poor linearity in a dilution series of standards.

21.2.1 Before you remake your standards, first examine the sample introduction area, making sure you’re getting a consistent flow of sample through your pump tubing and that your connectors are not too tight.

21.2.2 Then check your nebulizer and injector for visible build up. If build up is present, clean in a dilute nitric acid (HNO_3) solution for about 10-15 minutes.

21.2.3 Also examine your torch, making sure it is also reasonably clean. Lastly, check the argon tank to determine that it is not running on empty. If everything is satisfactory, then remake standards.

21.2.4 If problems persist, try a second source of standards to determine if your initial set of standards has gone bad.

21.2.5 Bubbles are collecting in the back area of the nebulizer (glass type).

21.2.6 The reason why bubbles form in this back area is because the pump tubing is not inserted deeply enough into the cavity of the nebulizer. Cut the tip of the pump tubing to be inserted into the nebulizer at a roughly 45º angle, preferably with a razor blade to obtain a nice, clean cut. Dip the cut end into a wetting agent such as dilute Triton X solution, and start to insert into the nebulizer. Using moderate pressure, begin to work the pump tubing into the nebulizer while twisting the tubing. The twisting action causes the tubing to gradually decrease in diameter, making it easier to insert deeply into the cavity.

21.3 Hard instrument failure (software related). These are generally problems associated with the software communication with the instrument.

21.3.1 Exit out of the program. Shut down the PC that is linked to the instrument itself and restart.

21.3.2 During the PC reboot process, locate the reset button(s) on the front and/or back of the instrument and depress them.

21.3.3 Enter back into the program and continue your analysis.

21.3.4 This generally will fix this type of problem, but if you encounter additional problems of this type, then a service call may be necessary for more advanced troubleshooting advice.

21.4 Peristaltic pump occasionally stutters or stops. This problem may be hard to notice since this is a gradual wearing of the belt that attaches to the pump motor and turns the rollers themselves.

21.4.1 Replace the belt if you have an available spare. If you do not have a replacement, a service call needs to be made. A service person will generally come out and install the belt but on occasion, based on your mechanical abilities, they may ship the part to you and have you perform the installation.

22. Safety

22.1 Standards and Reagents
The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound shall be treated as a potential health hazard. Special care shall be taken when handling the high-concentration acids and oxidizing reagents used for sample digestion. All digestions must be conducted in a properly functioning fume hood. The use of personal protective equipment (gloves, lab coats and safety glasses) is required.

22.2 A reference file of Safety Data Sheets (SDS) is made available to all personnel involved in this process, and is located at by the following link https://msdsmanagement.msdsonline.com/c0ce0b0a-17d3-4f3c-afc6-25352729b299/ebinder/?nas=True.

22.3 Samples

22.3.1 Although sample check-in should be notified of any hazardous samples, samples shall always be considered as “unknowns”.

22.3.2 The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples.

22.4 Equipment

22.4.1 ICP Radio Frequency (RF) Generator – The RF generator used to induce the atomic plasma produces a high energy radio emission. The electrical requirements for this equipment are substantial. The RF generator must only be serviced by those trained specifically for service and repair of the instrument.

22.4.2 ICP RF Coil – The wound coil around the top of the torch produces a high energy, oscillating radio frequency field. The field is substantial and may interfere with surrounding electronics including implanted medical devices. Those individuals with such devices (i.e. pacemakers) must stay clear of this instrument while in operation.

23. Waste Management

23.1 Procedures for handling waste generated during this analysis are addressed in S-GB-W-001, *Waste Handling and Management.*

23.2 In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention

24.1 The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1 Pace Analytical Services, LLC Quality Manual, most current version.

25.2 The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version

25.3 USEPA, SW-846, Method 6010C Revision 3, "Inductively Coupled Plasma Atomic Emission Spectrometry", February 2007.

25.4 USEPA, SW-846, Method 3010A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectrometry", December 1996.

25.5 USEPA, SW-846, Method 3050B, "Acid Digestion of Sediments, Sludges, and Soils", December 1996.

25.6 USEPA, 200.7 Revision 4.4, "Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasm-Atomic Emission Spectrometry", 1994.

25.7 Standard Methods for the Examination of Water and Wastewater, 2340B-2011 Hardness by Calculation.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, ETC.

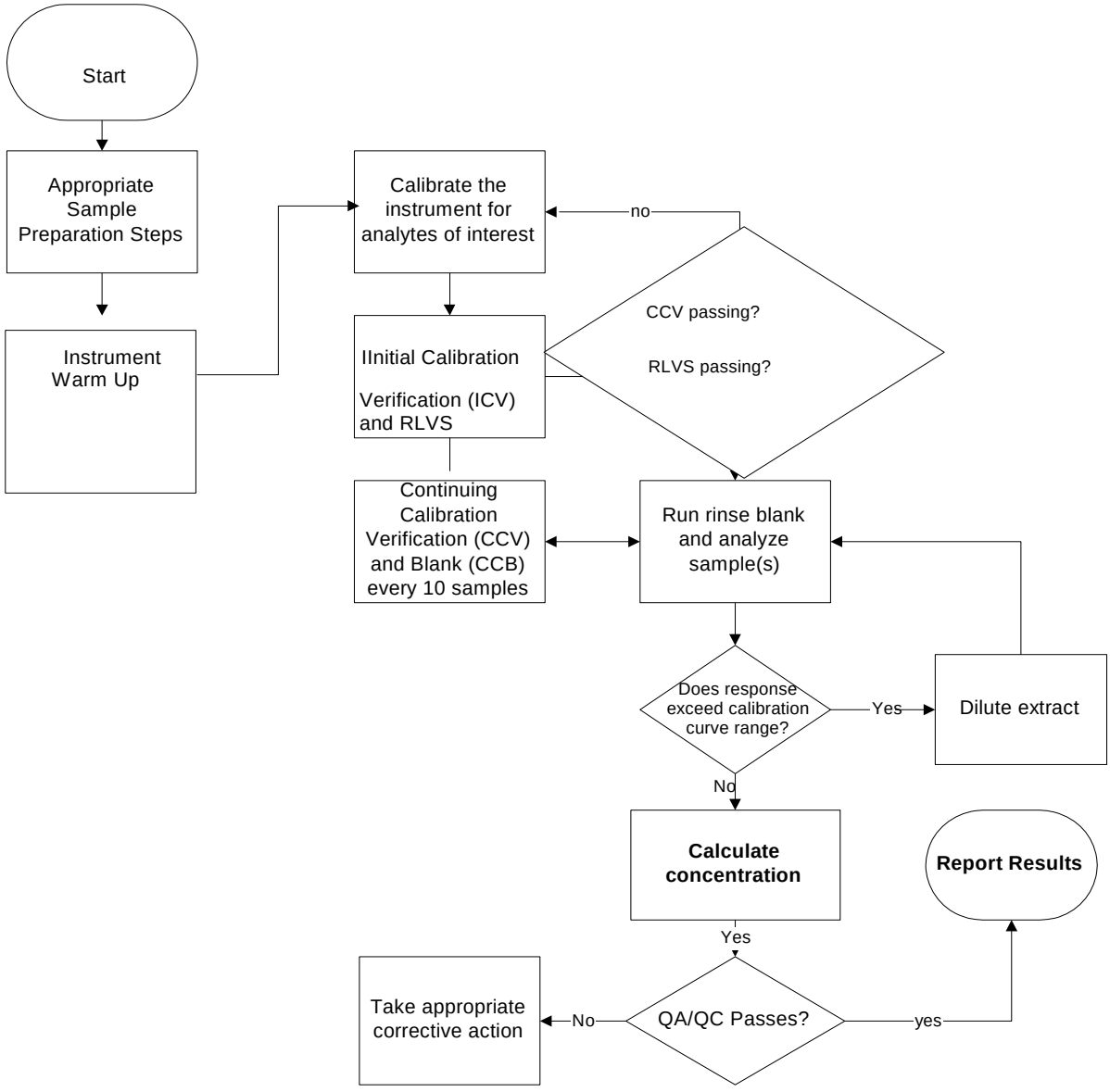
26.1 **Attachment I** – ICP Flowchart

27. Revisions

Document Number	Reason for Change	Date
S-GB-M-005-Rev.06	Throughout Document: Updated to current format of SOP: S-GB-Q-017 *Preparation of SOPs*, and updated to current SOP references. Throughout Document: Added information for 200.7 and Hardness by 2340B and 6010. Removed: Attachments with Preparation Methods Section 25: Added TNI and PASI QM references. Table 7.1: Updated Temperature to ≤6°C from 4±2°C.	11Nov2014
S-GB-M-005-Rev.07	Throughout Document: Updated from MDL to LOD, RL to LOQ; changed from ppm to mg/L. Signature Page: Updated from Inc. to LLC. And updated QM name. Section 3.1: Updated low standards. Section(s) 9.1/9.2: Deleted digestion equipment, updated vendor/catalog information. Section(s) 10.4, 13.3.3: Updated ICSAB requirement for non-spiked elements. Section 11: Added Rinse time, Nebulizer flow rate and Solution Uptake rates. Section 12.1.5: Added information for dissolved samples. Section 13: Added information on Duplicates, added Section 13.4.7. Section 27: Removed previous revision documentation which can be found in the previous SOP.	09Jan2017
S-GB-M-005-Rev.08	Section 12.2.2: Added discussion for analyst steps when possible carry-over is present. Section 18.5: IEC information updated.	21Jun2017

Attachment I

ICP Flowchart



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STANDARD OPERATING PROCEDURE

DETERMINATION OF SEMI-VOLATILE ORGANICS BY GC/MS

Reference Methods: EPA SW-846 Method 8270C / EPA 625

Local SOP Number:	S-GB-O-049-Rev.07
Effective Date:	Date of Final Signature
Supersedes:	S-GB-O-049-Rev.06
SOP Template Number:	SOT-ALL-O-001-rev.01

APPROVALS

Nils Melberg, Laboratory General Manager — Date: 06/21/17

Kate Verbeten, Laboratory Quality Manager — Date: 6/21/17

Chris Haase, Laboratory Department Manager — Date: 6/21/17

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date

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1. Purpose/Identification of Method

This Standard Operating Procedure (SOP) documents the procedures used by PASI – Green Bay to determine the concentration of Semi-volatile Organic Compounds (SVOCs) in environmental samples. The laboratory utilizes GC/MS and bases these documented procedures on those listed in EPA SW-846 Method 8270C/ EPA 625. The Green Bay laboratory currently processes water samples by automated separatory funnel using Method SW846 3510C, soil samples by Microwave Extraction using Method SW846 3546 and biota samples by soxhlet extractor using Method SW846 3540C. The latest revision of Pace's SOPs S-GB-O-053 *Separatory Funnel Extraction of Water Samples for Semivolatile Analysis* (most current revision or replacement), S-GB-O-045 *Microwave Extraction for the Determination of Polynuclear Aromatic hydrocarbon, Base/Neutral/Acids, and Total Petroleum Hydrocarbons on Solid Matrices* (most current revision or replacement), and S-GB-O-033 *Extraction of Biological Samples for Base Neutral/Acid and PAH-SIM Analysis* (most current revision or replacement) for these extraction techniques are available from the quality office.

2. Summary of Method

2.1. Sample extracts are prepared for analysis by an appropriate sample preparation method. The semivolatile organic compounds are introduced into the gas chromatograph (GC) by injecting an aliquot of the sample extract. The GC conditions are programmed to separate the analytes. The GC effluent is directly introduced to a mass spectrometer (MS) for both identification and quantification of analytes. Analytes are identified by comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using a multi-point calibration curve.

3. Scope and Application

3.1. This procedure may be used to determine concentrations of neutral, acidic, and basic semivolatile organic compounds in extracts prepared from many types of water samples, soil samples and wastes. Analytes must be soluble in dichloromethane and amenable to capillary gas chromatography. Specific compound classes include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols. A list of applicable compounds is shown in Table 11.1 Calibration Standard Compound Concentrations. Pace Reporting Levels (PRLs) are also shown for water and soil samples. PRLs are subject to change based on current analytical system performance and actual sample matrices.

3.2. This method is applicable to most water and solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, and other solid samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix related modifications must be documented within the analytical data.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of semi-volatile configured GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.4. This method cannot be substituted for other similar published methods where permit or regulatory compliance is required.

4. Applicable Matrices

4.1. This SOP is applicable to soils/sediments, solid wastes, tissue, wipes and aqueous matrices.

5. Limits of Detection and Quantitation

5.1. The reporting limit (LOQ) for all analytes is listed in Table 11.1 for the listed methods. All current MDLs are listed in the LIMS and are available by request from the Quality Manager.

6. Interferences

6.1. Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

6.2. Matrix interferences may result from materials co-extracted from some samples.

6.3. Significant phthalate contamination may result at any time if consistent quality control is not practiced. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

6.4. Contamination by carryover can occur when high concentration extracts are analyzed prior to low concentration extracts. The contamination may also cause degradation of labile analytes. Whenever carryover is suspected, the affected extracts should be re-analyzed. If significant degradation of the GC/MS systems is suspected, system performances samples should be analyzed and corrective action taken as needed.

7. Sample Collection, Preservation, Shipment and Storage

7.1. **Table 7.1 – Sample Collection, Preservation, Storage, and Hold time**

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	One 1L amber glass Samples to be analyzed for EPA 625 must be checked for residual chlorine. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well.	None	0-<6°C	7 days
Soil/Solid (non-aqueous)	One 8oz wide glass jar	None	0-<6°C	14 days
Biota	-	None	≤ -10°C until extraction	1 year when frozen
TCLP	One 1L Amber Glass	None	0-<6°C	TCLP Leachates must be solvent extracted within 7 days of the completion of the process.
Extracts	2 mL amber glass vials	None	≤ -10°C	40 days

8. Definitions

Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary.

8.1. **Toxicity Characteristic Leaching Procedure (TCLP) –** An extraction procedure used to determine if a sample is acceptable for upland disposal. The extraction procedure is meant to simulate the leaching of contaminants under the environmental conditions typically found in a landfill.

8.2. **Run Sequence Log** – A logbook that lists all injections and analyses performed on a particular piece of equipment regardless of the use of the data collected from each analysis.

8.3. **Tune Period** – The period after the DFTPP instrument tune check within which analyses may be performed.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. **Table 9.1 - Instrumentation**

Analytical Instrument/Peripherals	EPIC Pro Name	Serial Number
HP 5890 Series II GC	40MSS1	3336A57925
HP 5972 Mass Selective Detector	40MSS1	3501A02320
HP 7673 AutoSampler Tray	40MSS1	3526A39072
HP 7673 Injector	40MSS1	3009A20936
HP Controller	40MSS1	3526A02233
Alcatel 2005 Rough Pump	40MSS1	265402
HP 5890E GC	40MSS6	3310A49571
HP 5972A Mass Selective Detector	40MSS6	3524A03107
HP 18596A AutoSampler Tray	40MSS6	2920A10670
HP 6890 Injector	40MSS6	US0000692
HP 7673 Controller	40MSS6	3113A25880
Edwards E2M2 Rough Pump	40MSS6	53747
Agilent 7890A GC	40MSS8	CN10705029
Agilent 5975C Mass Selective Detector	40MSS8	US71226404
HP Autosampler tray G2614A	40MSS8	US93806114
HP injector G2613A	40MSS8	US93909562
Edwards E2MS Rough Pump	40MSS8	69070
Agilent 7890B	40MSSA	CN15483197
Agilent 5977A Mass Selective Detector	40MSSA	US1422L235
Agilent Autosampler tray G4514A	40MSSA	CN13330090
Agilent injector G4513A	40MSSA	CN14510236
Edwards E2M2 Rough Pump	40MSSA	DUO25

9.2. **Table 9.2 - Chromatography Supplies**

Item	Vendor	Model / ID	Catalog #	Description
Analytical Column	Restek	XTI-5 w/ Integraguard	12223-124	30 m, 0.25 mm ID, 0.25 df
Analytical Column	Phenomenex	ZB Semivolatiles Guardian	7HG-G027-11-GGC	20m, 0.18 mm ID, 0.18 df
Fluorocarbon O-rings	Restek		20377	
Vespel/Graphite Ferrules	Restek		20229	1/16" x 0.4 mm ID
Gooseneck Splitless Liner	Restek		20800	4 mm x 6.5 x 78.5 for Aligent GCs
Uniliner	Restek	Drilled Uniler	20771	w/hole in bottom
Inlet Seals	Restek	Dual Vespel Ring Inlet Seals	212389	Stainless steel

9.3. **Table 9.3 - Glassware**

Glassware	Description	Vendor / Item # / Description
Volumetric Flasks	10mL, 25mL, 50mL	Class A
Glass Storage Vials	5mL, 10mL, 12mL, with Teflon-lined screw caps	MG Scientific / T102-3-INV, T102-1-INV V138-19, B510-1
Glass Autosampler Vials	2.0mL with Teflon-lined crimp or screw caps	MG Scientific / V300-3 / V300-20N

9.4. **Table 9.4 - General Supplies**

Supply	Description	Vendor/Item #
Gas tight syringes	10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL, as needed, Hamilton or equivalent.	Fisher Scientific/Various
Pipettes	Borosilicate Glass 9" Pipette	MG Scientific / D200-9

10. Reagents and Standards

10.1. **Table 10.1 – Reagents**

Reagent/Standard	Concentration/ Description	Manufacturer/Vendor/Item #
Methylene Chloride (Dichloromethane)	Pesticide Grade or equivalent / $MeCl_2$	MG Scientific / # 9266-8P
Methanol	Purge and Trap Grade or equivalent / MeOH	Burdick & Jackson / VWR Scientific / 232-1
Acetone	Pesticide Grade or equivalent/ Acetone	Burdick and Jackson / 010-4

10.2. **Table 10.2 - Standard Definitions**

Standard	Description	Comments
Tune Standard	Decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine solution in dichloromethane used to verify ion response ratios and system inertness prior to analysis	Must inject no more than 50ng on column
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	Method requires a minimum of 5 levels
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	
Second Source Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the accuracy of the calibration curve.	
Internal Standard	A solution added to all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard is used to adjust response ratios to account for instrument drift.	1,4 Dichlorobenzene-d4 Naphthalene-d_8 Acenaphthene-d_{10} Phenanthrene-d_{10} Chrysene-d_{12} Perylene-d_{12}
Surrogate Standard	A solution added to all samples, spikes, control samples, and method blanks prior to analysis.	Nitrobenzene-d_5 2-Fluorobiphenyl Terphenyl-d_{14} Phenol-d_6 2-Fluorophenol 2,4,6-Tribromophenol
Spiking Standard	This solution contains 70 target analytes and should not be prepared from the same standards as the calibration standards.	

10.3. **Table 10.3 - Standard Storage Conditions**

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date for unopened ampulated standards. ▪ Stock standards must be replaced 1 year after ampule is opened or on expiration date, whichever is sooner.	▪ Manufacturer's recommended storage conditions ▪ When standard is opened, record all information in the standard logbook.
Intermediate and Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ 1 year from preparation or the expiration date listed for the stock source, whichever is sooner. ▪ Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	▪ Store in amber vials with Teflon lined screw caps ▪ <-10 like sample extracts ▪ If stock source conditions conflict, store according to method requirements.

10.4. **Standard Sources**: Standards are prepared from commercially available multi-compound stock solutions and neat materials by multiple dilutions. The sources of the stock solutions and neat

materials, recipes for preparing dilutions and working standards, and concentrations for all compounds are presented in table 9.4. All intermediate standards are prepared using dichloromethane and stored in glass vials with Teflon lined caps or as recommended by the standard manufacturer.

10.5. **Preparation Procedures:**

10.5.1. **Internal Standard Stock solution:** Restek brand Internal Standard Mix, 4000µg/mL, catalog #31006 (contains six internal standards: acenaphthene-d10; chrysene-d12; 1,4-dichlorobenzene-d4; naphthalene-d8; perylene-d12; and phenanthrene-d10), or equivalent. Add 10µL of internal standard solution to 1000µL of every standard, sample, and QC sample injected.

10.5.2. **Surrogate Standard stock solutions:** Restek brand Base Neutral surrogate mix, 5000µg/mL, catalog #31082 (contains four surrogate standards: 2-fluorobiphenyl; nitrobenzene-d5; p-terphenyl-d14; 1,2-Dichlorobenzene-d4 (advisory)). Restek brand Acid surrogate mix, 7500µg/mL, catalog #31083 (contains four surrogate standards: 2-fluorophenol; phenol-d6; 2,4,6-tribromophenol; 2-chlorophenol-d4 (advisory)), or equivalent.

10.5.3. **Surrogate Standard working solution (for extractions)**: dilute 5.0mL of both the Restek Base Neutral stock surrogate solution (#31082) and the Restek Acid stock surrogate solution (#31083) to 50mL with Acetone, or equivalent. This gives a final concentration of 500µg/mL per Base Neutral surrogate compound and 750µg/mL per Acid surrogate compound. The extraction analyst spikes each water and soil sample with 100µL of this working solution.

10.5.4. **DFTPP tuning solution:** dilute 1250µL of Supelco DFTPP stock standard (catalog #47548-U; 1000µg/mL) to a total volume of 25mL with methylene chloride for a final concentration of 50µg/mL, or equivalent. The stock standard also contains 4,4'-DDT, benzidine, and pentachlorophenol for assessing column degradation. Information for the standards preparation and expiration dates are affixed to the outside of the vial, and is easily accessible through Epic Pro LIMS. The standard material will be kept in a freezer at -10°C.

10.5.5. **Initial Calibration curve standards**: the following four stock standards, or equivalent, are used to prepare the initial calibration curve:

10.5.5.1 8270 Custom Mix 1, Restek Custom Mix at 200ug/mL cat.#52939

10.5.5.2 1,4-Dioxane, Restek, 2000µg/mL, catalog #30287

10.5.5.3 2,3,4,6-Tetrachlorophenol, AccuStandard, 2000µg/mL, catalog #A-029S-D-10X

10.5.5.4 1,2,4,5-Tetrachlorobenzene, Absolute Standards, 1000µg/mL, catalog #70274

10.5.5.5 **Initial Calibration Intermediate Standard:** Dilute 3mL of 200µg/mL Restek 8270 Custom Mix 1, 300µL of the 2000µg/mL 1,4-Dioxane solution, 300 µL of the 2000 µg/mL 2,3,4,6-Tetrachlorophenol solution, and 600 µL of 1000µg/mL 1,2,4,5-Tetrachlorobenzene to 5.0mL with dichloromethane, or equivalent. The resulting intermediate standard has a concentration of 120mg/L for each compound.

10.5.6. **Working Standard Preparation**: Working calibration standards are prepared in dichloromethane or a water soluble solvent. Standards made for direct analysis on the GC/MS are made in dichloromethane. Standards made for addition into samples as part of the preparation are made into Acetone. Depending on the volume of each solution needed, the standards are brought to volume in volumetric flasks or prepared in smaller, glass vials and brought to volume by additions of solvent with micro syringes.

10.5.6.1 **Initial Calibration Verification stock standards (second-source)**

10.5.6.1.1 O2si, 200ug/mL, Catalog #113881-05.

10.5.6.1.2 n-Nitrosodiphenylamine, Supelco, 5000ug/mL, Catalog #46702-U.

10.5.6.1.3 Supelco, 1,4-Dioxane, catalog #48367, 2000µg/mL.

10.5.6.1.4 Absolute Standards, 2,3,4,6-tetrachlorophenol, catalog #92389, 5000µg/mL, or equivalent.

10.5.6.1.5 Supelco, 1,2,4,5-Tetrachlorobenzene, catalog #40177, 1000µg/mL.

10.5.6.2 **Initial Calibration Verification working standard (second source):** Dilute 250µL of the custom 8270 second source standard #113881-05, 10µL of 2,3,4,6-Tetrachlorophenol #560028, 25µL of 1,4-Dioxane #48367, 50µL of 1,2,4,5-Tetrachlorobenzene #40177, 10uL of 5000ug/mL n-Nitrosodiphenylamine, 10uL of 5000ug/mL B/N surrogate mix, 6.7uL of 7500ug/mL Acid surrogate mix and 10µL of the stock internal standard solution (9.5.1) to 1mL with dichloromethane, or equivalent. This gives a final concentration of 50ppm.

10.5.6.3 **LCS/MS Standard working solution:** Supelco 70 Component Custom MCS Mix catalog #861389-U, 200µg/mL. Supelco n-Nitrosodiphenylamine, catalog #46702-U, 5000µg/mL, or equivalent. The extraction analyst spikes each LCS/LCSD and matrix spike sample with 250µL of the LCS mix and 10µL of the n-NDPA solution. This produces a concentration of 50µg/mL.

10.5.6.4 **Other calibrations**: Other compounds are analyzed per client requests. Curves are prepared at levels similar to those of the standards above. The calibration standards and the second source standards are as follows: Calibration Standards, Benzidine, Calibration Standard, Supelco Catalog #40005, 5000µg/mL. Second Source, Restek, catalog #31441, 1000µg/mL; EPA CLP SOW OLM4 mix, Calibration Standard, Supelco Catalog#47514-U, 2000µg/mL. Second Source, Absolute Standards, catalog #19253, 2000µg/mL, or equivalent. Minnesota Phenols Samples required Calibration Standard Supelco 500ug/mL, cat.#LC12745, o2si, catalog #114055-05, 500 µg/mL. Phenol and 345-trichlorophenol, first source, Absolute Standards, second source; o2Si

10.5.6.5

10.5.7. Store at -10°C or less in amber Teflon-sealed containers. The solutions should be checked frequently for stability.

10.6. **Calibration Standard Preparation**: Calibration standards are made into dichloromethane for the purpose of direct analysis by the analytical instrumentation. The standards must be made in a volumetric fashion. Several alternatives exist but the method employed by Pace – Green Bay utilizes glass autosampler vials according to the following procedure. The individual standards can be made according to the details provided in table 10.3.

Table 10.4 – Working Standard Dilutions and Concentrations

Standard	Standard(s) Amount	Solvent	Solvent Volume	Final Total Volume	Final Concentration
Calibration Std 1	41.5µL	Dichloromethane	958.5µL	1010µL	5ppm
Calibration Std 2	83µL	Dichloromethane	917µL	1010µL	10ppm
Calibration Std 3	209µL	Dichloromethane	791µL	1010µL	25ppm
Calibration Std 4	417µL	Dichloromethane	583µL	1010µL	50ppm
Calibration Std 5	667µL	Dichloromethane	333µL	1010µL	80ppm
Calibration Std 6	833µL	Dichloromethane	167µL	1010µL	100ppm
Calibration Std 7	1000µL	Dichloromethane	0µL	1010µL	120ppm
Continuing Calibration Verification Standard	417µL	Dichloromethane	583µL	1010µL	50ppm

10.7. Traceability of Calibration Standards—The calibration standards purchased from vendors have been manufactured according to the following guidelines

10.7.1. Identity of neat material verified by GC/MS

10.7.2. Purity of neat material determined by GC/FID or GC/ECD. Correction for impurities is made when purity is less than 97%. Standards are prepared gravimetrically to a precision of 0.5%. All weights are traceable to NIST.

10.7.3. Analyte concentration verified by capillary gas chromatography. Standards tested for stability and homogeneity.

10.7.4. Standards are expiration dated.

10.8. Standard Labeling—All working calibration standards will have a label attached to the bottle identifying the following (Epic pro standard labels do not contain all the following)

10.8.1. Name of Solution

10.8.2. PASI, LLC. Standard ID Number

10.8.3. PASI, LLC. Lab Lot ID (for Stock standards and reagents)

10.8.4. Preparation Date

10.8.5. Preparer's initials

10.8.6. Concentration

10.8.7. Expiration Date

11. Calibration and Standardization

11.1. **Tune Verification –** The mass spectrometer tune status must be verified prior to initial calibration and at the beginning of each analytical sequence. If the current tune status does not meet the ion ratio criteria in the method (see section 12.2), follow the equipment manufacturers' instructions for re-tuning the mass spectrometer. The tune status must be verified after the tuning procedures. Refer to section 12.2 for details on the analysis and evaluation of this standard.

11.2. **Initial Calibration:**

11.2.1. **Analysis of Standards**: An initial calibration curve using a minimum of five points is analyzed prior to analyzing client samples. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values. Refer to table 11.1 for compound concentrations.

Table 11.1: Laboratory PQL and Calibration Standard Compound Concentrations

Analyte	PQL water (µg/L)	PQL soil (µg/kg)	PQL Biota (µg/kg)	Std 1 µg/L	Std 2 µg/L	Std 3 µg/L	Std 4 µg/L	Std 5 µg/L	Std 6 µg/L	Std 7 µg/L
Acenaphthene	5.0	167	330	5.0	10	25	50	80	100	120
Acenaphthylene	5.0	167	330	5.0	10	25	50	80	100	120
Aniline	5.0	167	N/A	5.0	10	25	50	80	100	120
Anthracene	5.0	167	330	5.0	10	25	50	80	100	120
Benz(a)anthracene	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(a)pyrene	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(b)fluoranthene	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(g,h,i)perylene	5.0	167	330	5.0	10	25	50	80	100	120
Benzo(k)fluoranthene	5.0	167	330	5.0	10	25	50	80	100	120
Benzoic acid	10	330	N/A	5.0	10	25	50	80	100	120
Benzyl alcohol	10	330	N/A	5.0	10	25	50	80	100	120
4-Bromophenylphenyl ether	5.0	167	330	5.0	10	25	50	80	100	120
Butylbenzylphthalate	5.0	167	330	5.0	10	25	50	80	100	120
Carbazole	5.0	167	330	5.0	10	25	50	80	100	120
4-Chloro-3-methylphenol	5.0	167	330	5.0	10	25	50	80	100	120
4-Chloroaniline	10	333	330	5.0	10	25	50	80	100	120
bis(2-Chloroethoxy)methane	5.0	167	330	5.0	10	25	50	80	100	120
bis(2-Chloroethyl) ether	5.0	167	330	5.0	10	25	50	80	100	120
bis(2-Chloroisopropyl) ether	5.0	167	330	5.0	10	25	50	80	100	120
2-Chloronaphthalene	5.0	167	330	5.0	10	25	50	80	100	120
2-Chlorophenol	5.0	167	330	5.0	10	25	50	80	100	120
4-Chlorophenylphenyl ether	5.0	167	330	5.0	10	25	50	80	100	120
1,2-Diphenylhydrazine	5.0	167	N/A	5.0	10	25	50	80	100	120
Chrysene	5.0	167	330	5.0	10	25	50	80	100	120
Dibenz(a,h)anthracene	5.0	167	330	5.0	10	25	50	80	100	120
Dibenzofuran	5.0	167	330	5.0	10	25	50	80	100	120
1,2-Dichlorobenzene	5.0	167	330	5.0	10	25	50	80	100	120
1,3-Dichlorobenzene	5.0	167	330	5.0	10	25	50	80	100	120
1,4-Dichlorobenzene	5.0	167	330	5.0	10	25	50	80	100	120
3,3'-Dichlorobenzidine	10	330	330	5.0	10	25	50	80	100	120
2,4-Dichlorophenol	5.0	167	330	5.0	10	25	50	80	100	120
Diethylphthalate	5.0	167	330	5.0	10	25	50	80	100	120
2,4-Dimethylphenol	5.0	167	330	5.0	10	25	50	80	100	120
Dimethylphthalate	5.0	167	330	5.0	10	25	50	80	100	120
Di-n-butylphthalate	5.0	167	330	5.0	10	25	50	80	100	120
4,6-Dinitro-2-methylphenol	5.0	333	670	5.0	10	25	50	80	100	120
2,4-Dinitrophenol	10	333	670	5.0	10	25	50	80	100	120
2,4-Dinitrotoluene	5.0	167	330	5.0	10	25	50	80	100	120
2,6-Dinitrotoluene	5.0	167	330	5.0	10	25	50	80	100	120
Di-n-octylphthalate	5.0	167	330	5.0	10	25	50	80	100	120
bis(2-Ethylhexyl)phthalate	5.0	167	330	5.0	10	25	50	80	100	120
Fluoranthene	5.0	167	330	5.0	10	25	50	80	100	120
Fluorene	5.0	167	330	5.0	10	25	50	80	100	120
Hexachloro-1,3-butadiene	10	333	330	5.0	10	25	50	80	100	120
Hexachlorobenzene	5.0	167	330	5.0	10	25	50	80	100	120
Hexachlorocyclopentadiene	5.0	167	330	5.0	10	25	50	80	100	120
Hexachloroethane	5.0	167	330	5.0	10	25	50	80	100	120
Indeno(1,2,3-cd)pyrene	5.0	167	330	5.0	10	25	50	80	100	120
Isophorone	5.0	167	330	5.0	10	25	50	80	100	120

Analyte	PQL water (µg/L)	PQL soil (µg/kg)	PQL Biota (µg/kg)	Std 1 µg/L	Std 2 µg/L	Std 3 µg/L	Std 4 µg/L	Std 5 µg/L	Std 6 µg/L	Std 7 µg/L
2-Methylnaphthalene	5.0	167	330	5.0	10	25	50	80	100	120
2-Methylphenol	10	333	330	5.0	10	25	50	80	100	120
3&4-Methylphenol	5.0	167	330	5.0	10	25	50	80	100	120
Naphthalene	5.0	167	330	5.0	10	25	50	80	100	120
2-Nitroaniline	5.0	167	330	5.0	10	25	50	80	100	120
3-Nitroaniline	5.0	167	670	5.0	10	25	50	80	100	120
4-Nitroaniline	10	333	670	5.0	10	25	50	80	100	120
Nitrobenzene	5.0	167	330	5.0	10	25	50	80	100	120
2-Nitrophenol	5.0	167	330	5.0	10	25	50	80	100	120
4-Nitrophenol	10	333	670	5.0	10	25	50	80	100	120
N-Nitrosodimethylamine	5.0	167	330	5.0	10	25	50	80	100	120
N-Nitroso-di-n-propylamine	5.0	167	330	5.0	10	25	50	80	100	120
N-Nitrosodiphenylamine	5.0	333	330	5.0	10	25	50	80	100	120
Pentachlorophenol	10	330	670	5.0	10	25	50	80	100	120
Phenanthrene	5.0	167	330	5.0	10	25	50	80	100	120
Phenol	5.0	167	330	5.0	10	25	50	80	100	120
Pyrene	5.0	167	330	5.0	10	25	50	80	100	120
Pyridine	5.0	167	330	5.0	10	25	50	80	100	120
1,2,4-Trichlorobenzene	5.0	167	330	5.0	10	25	50	80	100	120
2,4,5-Trichlorophenol	5.0	167	670	5.0	10	25	50	80	100	120
2,4,6-Trichlorophenol	5.0	167	330	5.0	10	25	50	80	100	120
1,4-Dioxane	10	330	N/A	5.0	10	25	50	80	100	120
1,2,4,5-Tetrachlorobenzene	5.0	167	N/A	5.0	10	25	50	80	100	120
2,3,4,6-Tetrachlorophenol	10	167	N/A	5.0	10	25	50	80	100	120
Acetophenone	10	333	N/A	5.0	10	25	50	80	100	N/A
Atrazine	10	333	N/A	5.0	10	25	50	80	100	N/A
Benzaldehyde	10	333	N/A	5.0	10	25	50	80	100	N/A
Benzidine	50	1670	N/A	5.0	10	25	50	80	100	N/A
Caprolactam	10	333	N/A	5.0	10	25	50	80	100	N/A
Biphenyl	10	333	N/A	5.0	10	25	50	80	100	N/A

11.2.2. An analyte must be present and calibration curve in control in order to be reported on the target analyte list. Analytes identified by mass spectral match but not present and in control in the calibration table may be reported as Tentatively Identified Compounds (TICs). Guidelines for identification are listed in Section 12.15. Results for these TICs should be reported only on a present/absent basis. However, quantitative results may be reported provided they are qualified as estimated values.

11.2.3. Calibration Response Factors: Response factors (RF) establish the relationship of the instruments response in comparison with the concentration of any given analyte. The RF includes the concentration and response of the internal standard as well. By relating the IS concentration and response in an inverse manner, the target analyte concentration is adjusted to account for drift in the instrument on a per injection basis. As instrument response increases as indicated by the response of the internal standard, the concentration of the target is mathematically decreased, and vice versa.

11.2.4. To calculate the RF for any given calibration standard (or calibration verification standard), tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound

relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation:

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

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_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L).

11.2.5. Most, if not all modern chromatography data systems are capable of calculating this factor and using it to quantify analyte concentrations. The 8270C method has minimum requirements that these response factors must meet in order to be considered valid. The method uses a subset of the target analyte list to evaluate the performance of the system. These compounds are referred to as the System Performance Check Compounds or the SPCCs. The SPCCs serve as an indicator of instrument sensitivity and, by meeting a minimum value, ensure that the laboratory has adequate sensitivity to analyze and reliably report data for environmental samples.

11.2.6. **Calibration Curve Fit**: The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. The curve is produced in several ways depending on the nature of the "goodness of fit".

11.2.7. **Average Response Factor (ARF)**: The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. It is in the most basic sense, a linear regression that is forced through zero at the origin. Because of its simplicity and the interception of the y axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of the ARF (see Table 11.2):

$$\%RSD = \left(\frac{SD \times 100}{ARF}\right)$$

Where:

SD = Standard deviation of the averaged RFs for a given compound

11.2.8. The average response factor is also used to diagnose the integrity of the chromatography system as it relates to calibration linearity. The ***Calibration Check Compounds (CCCs)*** are a subset of the target analyte list that must meet specific criteria (see Table 11.2) for the calibration to be acceptable. For the CCCs, the %RSD for each is compared to the method criteria. If that of any CCC exceeds the criteria, the system needs to be inspected for potential sources of errors and recalibrated.

11.2.9. **Linear Regression**: The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y=ax+b where "a" is the slope of the line and "b" is the y intercept. In order to use this curve fit technique, a minimum of 5 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument is linear in nature but does not necessarily intercept the y axis at

the origin. However, because the linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve (see Table 11.2).

11.2.10. **Non-linear Regression**: The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument gradually decreases with increasing concentrations. Using this technique, an analyst may be able to generate calibration curves with correlation coefficients very close or equivalent to 1.000. However, because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. Likewise, high levels of contamination may not be able to be calculated due to regression equations with multiple intercepts of either axis on the calibration plot.

11.2.11. A calculation of the coefficient of determination (COD) is used to determine the acceptability of a non-linear regressed curve (see Table 11.2). Either the low or high calibration points may be dropped to meet linearity criteria provided the laboratory meets the minimum 5 calibration point requirements. Points within the center of the curve may not be dropped unless an obvious problem is discovered and documented and permission of the supervisor or the quality manager is obtained. The point must be dropped in its entirety. Re-analysis if performed should be within the same 12 hour time window and must occur within 8 hours of the original analysis.

11.3. **Calibration Verification**:

11.3.1. Low Level Calibration Check(CRDL): The lowest range of the calibration will be checked by either refitting the lowest calibration point against the calibration curve or re-analyzing the lowest calibration point. The CRDL must be checked before running any sample from MN and must meet a recovery of 60-140% of the expected value. Any compounds failing must be flagged in MN samples as failing to meet CRDL limits.

11.3.2. **Second Source Verification**: In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

11.3.3. Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification (ICV)***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the ICV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

$$\%\ Difference = \frac{(RFccv - AveRFcal)}{AveRFcal} * 100$$

$$\%\ Drift = \frac{(Result\ CCV - True\ Value\ CCV)}{True\ Value\ CCV} * 100$$

11.3.4. **Continuing Calibration Verification (CCV)**: As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***. The validity of the initial calibration is checked at the beginning of every analytical sequence and every 12 hours thereafter for as long as the instrument is analyzing samples and is accomplished by analyzing a midpoint calibration standard (CCV).

11.3.5. The values obtained from the analysis of the CCV are compared to the true values and a percent change calculated. The percent change must meet the method specified criteria for the analysis to proceed for an additional 12 hours.

11.3.6. The actual determination of change in instrument response is based on the type of curve fit used for each analyte. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the CCV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

$$\%\ Difference = \frac{(RFccv - AveRFcal)}{AveRFcal} * 100$$

$$\%\ Drift = \frac{(Result\ CCV - True\ Value\ CCV)}{True\ Value\ CCV} * 100$$

Table 11.2: Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Response Factor	%RSD ≤ 15%	If not met, try linear regression fit
	Linear Regression	r ≥ 0.99	If not met, try non-linear regression fit
	Non-linear Regression	COD ≥ 0.99	If not met, remake standards and recalibrate
System Performance Check Compounds (SPCCs)	N-Nitroso-di-n-propylamine Hexachlorocyclopentadiene 2,4-Dinitrophenol 4-Nitrophenol	Avg RF ≥ 0.05 Avg RF ≥ 0.05 Avg RF ≥ 0.05 Avg RF ≥ 0.05	Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, poor purging efficiency, and active sites in the column or chromatographic system.
Calibration Check Compounds (CCCs)	Acenaphthene 1,4-Dichlorobenzene Hexachlorobutadiene N-Nitrosodiphenylamine Di-n-octylphthalate Fluoranthene Benzo[a]pyrene 4-Chloro-3-methylphenol 2,4-Dichlorophenol 2-Nitrophenol Phenol Pentachlorophenol 2,4,6-Trichlorphenol	%RSD < 30%	%RSD for the calibration check compounds (CCC's) must be ≤30% regardless of curve fit used. If the CCCs are not included on a list of analytes for a project, and therefore not included in the calibration standards, then all compounds of interest must meet a ≤15% RSD criterion.
Second Source Verification Standard	Immediately after each initial calibration	% Drift ±30%	Acceptance criteria are ±30% for all analytes, with allowances for 5% of compounds at ±40%. See current revision of S-GB-Q-026. Additional client specific requirements for the analysis of contract samples requires that all compounds must be within ±20%.
Continuing Calibration Verification	Prior to the analysis of any samples and every 12 hours thereafter		If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back.
	SPCCs	Must meet response criteria listed above	
	Internal Standard RT	RT ± 30 sec	Use midpoint calibration standard as reference
	Internal Standard Response	50 – 200%	Use midpoint calibration standard as reference
	CCCs	RF ± 20% Diff.	Use for Avg RF calibration curves
		Result ± 20% Drift	Use for linear and non-linear calibration curves
	Non-CCC Targets	EPA 8270 Criteria: RF ± 50% Diff. Result ± 50% Drift EPA 625 Criteria: RF ± 20% Diff. Result ± 20% Drift	Some programs may require control over non-CCC target analytes. In the absence of specified criteria, use those listed

11.4. **Calibration Corrective Actions:**

11.4.1. Calibration Linearity Problems:

11.4.1.1 Check instrumentation/equipment condition. Document instrument maintenance in the logbook.

11.4.1.2 Perform another initial calibration.

11.4.1.3 No data can be reported.

11.4.1.4 Generate Non-Conformance Memo.

11.4.2. Second Source Verification Problems:

11.4.2.1 Check instrumentation/equipment condition. Document instrument maintenance in the logbook.

11.4.2.2 Perform another initial calibration.

11.4.2.3 No data can be reported.

11.4.2.4 Generate Non-Conformance Memo.

11.4.3. Continuing Calibration Verification Problems:

10.4.3.1. Reanalyze the original CCV standard to determine instrument consistency.

10.4.3.2. Prepare and analyze a new CCV standard to determine preparation consistency/standard integrity.

10.4.3.3. Document instrument maintenance.

10.4.3.4. Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

10.4.3.5. Complete recalibration of instrument.

10.4.3.6. If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

10.4.3.7. *Exceptions:* If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis.

12. Procedure

12.1. **Operating Parameters:** Configure the GC/MS system to match the following operating parameters based on instrument configuration. The parameters themselves are saved as a method on the chromatography data system. By loading the last method used, the instrument will auto-configure to match the parameters from the last time the system was operated under that method. Verify that the settings in the software match the appropriate configuration.

Table 12.1: Instruments and Operating Parameters

GC/MS Instrument 40MSS1	
GC: Hewlett Packard model 5890	MS: Hewlett Packard model 5972A
Operating Parameters:	Operating Parameters:
Initial Temp: 40°C	Acquisition mode: SCAN
Temp Program: hold 1.0 min at 40°C, ramp at 18°C/min to 100°C, then ramp at 15°C/min to 290°C, hold 5.95min, then ramp at 40°C/min to 320°C and hold for 1 min	Mass Range: 35-500
Final Temp: 320°C	
Transfer Line Temp: 300°C	
Column: Restek XTI-5 (30m; 0.25mm ID and 0.25µm film thickness)w/Integraguard	
Purge Flow: 40mL/min	
GC/MS Instrument 40MSSA	
GC: Agilent 7890B	MS: Hewlett Packard model 5977A
Operating Parameters:	Operating Parameters:
Initial Temp: 45°C	Acquisition mode: SCAN
Temp Program 45°C hold 1.00min, ramp at 30°C/min to 260°C hold for 0min, then ramp at 6°C/min to 295°C and hold for 0 min, then ramp at 25C/min to 325C and hold for 2min	Mass Range: 35-550
Final Temp: 325°C	
Transfer Line Temp: 300°C	
Column: Phenomenex ZB-Semivolatile Guardian 30 m, 0.25 ID(mm), 0.25 film thickness(mm)	
Split Ratio: L/minb 10:1	
GC/MS Instrument 40MSS8	
GC: Agilent 7890A	MS: Hewlett Packard model 5975
Operating Parameters:	Operating Parameters:
Initial Temp: 45°C	Acquisition mode: SCAN
Temp Program 45°C hold 1.00min, ramp at 30°C/min to 260°C hold for 0min, then ramp at 6°C/min to 295 °C and hold for 0 min,then ramp 25C/min to 325C and hold for 2 min.	Mass Range: 35-550
Final Temp: 325°C	
Transfer Line Temp: 300°C	
Column: Phenomenex ZB-Semivolatile Guardian 30 m, 0.25 ID(mm), 0.25 film thickness(mm)	
Split Ratio: 10:1	
GC/MS Instrument 40MSS6 used for Minnesota Phenols Samples	
GC: Hewlett Packard model 5890	MS: Hewlett Packard model 5972A
Operating Parameters:	Operating Parameters:
Initial Temp: 50°C	Acquisition mode: SCAN
Temp Program 50°C, ramp at 18°C/min to 150°C, then ramp at 3°C/min to 167°C , then ramp at 40°C/min to 320°C and hold for 2.5 min	Mass Range: 35-500
Final Temp: 320°C	
Transfer Line Temp: 300°C	
Column: Phenomenex ZB-Semivolatiles (30m; 0.25µm ID, 0.25 df)	
Split Flow: 100mL/min	

12.2. **Tune Verification**: At the beginning of each analytical sequence, prior to the analysis of any standards or samples, the mass spectrometer tune conditions must be verified. This is done by analyzing a standard containing DFTPP. The tune verification standard can be combined with the CCV standard provided that the amount of DFTPP introduced into the system meets the method criteria. For semi-volatile analysis, the system must also be verified for inertness. This is done simultaneously by the inclusion of DDT, benzidine and pentachlorophenol. DDT is used to verify breakdown conditions; benzidine and pentachlorophenol are used to check for tailing due to system activity.

12.2.1. After the analysis of this standard, the mass spectrum of DFTPP must be evaluated against the following criteria:

Mass (m/z)	Ion Abundance criteria
51	10.0-80.0% of m/z 198
68	<2.0% of m/z 69
69	Present
70	<2.0% of m/z 69
127	10.0-80.0% of m/z 198
197	<2.0% of m/z 198
198	Base peak, >50% of Mass 442
199	5.0-9.0% of m/z 198
275	10.0-60.0% of m/z 198
365	>1% of m/z 198
441	Present, but less than m/z 443
442	>50.0% of m/z 198
443	15.0-24.0% of m/z 442

12.2.2. To evaluate the tune spectra, following the operating instructions for the chromatography data system to access the data file and obtain mass spectra for DFTPP. If the software has a program or macro for automatically selecting the spectra and evaluating the response ratios, use this option. Otherwise, the spectra must be obtained in one of the following manners, in the listed order:

1. **Using an average of three scans, centered on the apex of the peak; or,**
2. **Using an average of all scans across the width of the peak, taken at half height; or,**
3. **Using an average of all scans taken across the width of the peak from baseline to baseline.**

A background scan taken immediately before but not including the peak must be subtracted.

12.2.3. Once obtained, evaluate the ion ratios against the criteria listed above. If the ratios meet the criteria, then analysis may proceed for 12 hours. The window for analysis is 12 hours from the injection date / time for the DFTPP tune verification. After that, the tune must be verified again to establish a new analytical window. The same Ion Abundance Criteria used for the DFTPP tune coupled with the initial calibration must be used for all subsequent analyses associated with that initial calibration.?

12.2.4. If the ratios do not meet the criteria, refer to the following corrective actions to address the problem: Any changes made to the system must be followed with the reanalysis of a tune verification standard. Any maintenance performed on the physical mass spec components requires recalibration. “Autotunes” may be performed as long as the following CCV meets all criteria for response, retention time and sensitivity.

12.3. **Tailing Factor Verification-** Benzidine and Pentachlorophenol should be present at their normal responses, and peak tailing should not be to an excess.

12.3.1. **Column performance test for base / neutrals –** At the beginning of each day that the base / neutral fraction is to be analyzed for benzidine, the benzidine tailing factor must be calculated. The benzidine tailing factor must be less than 3.0.

12.3.2. **Column performance test for acids –** At the beginning of each day that the acid fraction is to be determined, the pentachlorophenol tailing factor must be calculated. The pentachlorophenol tailing factor must be less than 5.0.

12.3.3. **Tailing factor calculation –** Refer to Attachment II: Tailing Factor Calculation.

12.3.4. The tailing factor of 3.0 for Benzidine and 5.0 for Pentachlorophenol must not be exceeded. If the tailing factor for either exceeds this amount, corrective action must be taken prior to the analysis of samples(unless all compounds required by samples analyzed after this tune and check meet Calibration Check Compound(CCC) limits). The tailing factor must be verified by the analysis of another tailing factor standard after corrective action is taken. Follow the following steps to return the system to an acceptable operating condition.

12.3.4.1 Perform front-end maintenance on the GCMS System.

12.3.4.2 Begin the run again by re-analyzing the DFTPP tune solution.

12.4. **Breakdown Verification-** The GC/MS system must be sufficiently inert such that DDT will not breakdown excessively while in the injection port. The inertness is assessed by calculating the percent breakdown of DDT into the products DDD and DDE. The calculation is performed as follows:

$$\%DDT\ Breakdown = \left(\frac{(DDD + DDE)}{(DDT + DDD + DDE)}\right) * 100$$

12.4.1. The % breakdown **must not exceed 20%.** If the breakdown of DDT exceeds this amount, corrective action must be taken prior to analysis of samples(unless all compounds required by samples analyzed after this tune and check meet Calibration Check Compound(CCC) limits. The breakdown must be verified by the analysis of another breakdown standard after corrective action is taken. Follow the following steps to return the system to an acceptable operating condition.

12.4.1.1 Perform front-end maintenance on the GCMS System

12.4.1.2 Begin the run again by re-analyzing the DFTPP tune solution.

12.5. **Calibration Verification**: After the instrument tune conditions are verified and the system meets tune criteria, the instrument must undergo calibration verification. If it has already been determined that the instrument needs to be recalibrated, follow the procedures listed in section 11.2 (Analysis of Standards). Otherwise, analyze a Continuing Calibration Verification Standard to determine the current calibration status.

12.6. If the CCV meets control criteria, the system is deemed to be in control and analysis of samples may commence. If the CCV does not meet control criteria, follow the corrective action procedures listed section 11.4.3 (Continuing Verification Problems). If the tune verification has been combined with the CCV, the 12 hour analysis window begins from the analysis date / time of the CCV.

12.7. *Note:* In situations where the instrument will run unattended (i.e., overnight), the analyst may load sequential CCVs in anticipation of that the first in the series may fail due to carry over from a previous sample. If so, the CCV must be evaluated according to the protocol set forth in the Quality Assurance Manual within the Equipment and Measurement Traceability section.

12.8. **Sample Preparation**-

12.8.1. **Water Samples**: Aqueous samples are prepared according to EPA 3510C. These procedures are contained in a separate standard operating procedure. Refer to SOP number S-GB-O-053 *Separatory Funnel Extraction of Water Samples for Semivolatile* (most current revision or replacement) for details on the preparation of aqueous samples.

12.8.1.1 Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10µL of the internal standard solution.

12.8.2. **Soil Samples**: Solid samples are prepared according to EPA 3546. These procedures are contained in a separate standard operating procedure. Refer to SOP number S-GB-O-045 *Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons, Base/Neutral/Acids, and Total Petroleum Hydrocarbons in Solid Matrices* (most current revision or replacement) for details on the preparation of soil or solid samples.

12.8.2.1 Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10µL of the internal standard solution.

12.8.3. **Biota Samples:** Biota samples are prepared according to EPA Method 3540C. These procedures are contained in a separate standard operating procedure. Refer to S-GB-O-033 *Extraction of Biological Samples for Base Neutral/Acid and PAH-SIM Analysis* (most current revision or replacement) for details on the preparation of biota samples.

12.8.3.1 Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 5µL of the internal standard solution.

12.9. **Dilutions**

12.9.1. Dilutions on sample extracts must be prepared in a volumetric fashion. Sample aliquots should be taken in volumetric syringes and brought to volume by the addition of solvent via an appropriate syringe. In the event a dilution is made to bring a target analyte into calibration range, the analyst should make a dilution such that the target analyte is roughly the equivalent of the mid calibration point whenever possible. If dilutions are made on extracts that already contain internal standards, a proportional aliquot of internal standard solution must be added to the diluted extract based on the volume of diluent used.

12.10. **Sample Analysis-**

12.10.1. GC/MS System Preparation

12.10.1.1 Operating Parameters – Set up the instrument parameters shown in Table 12.1

12.10.1.2 System Tuning and GC Performance Checks – Analyze the Tuning Solution and tune the mass spectrometer to meet the criteria shown in Section 12.2. Verify acceptable GC system performance as described in Section 12.2. Print out a tune report.

12.10.1.3 Batch Sequence – Generate a sequence to run a batch of samples.

Initial Calibration – The typical batch for initial calibration should include:

Tune Standard
Calibration Level 1
Calibration Level 2
Calibration Level 3
Calibration Level 4
Calibration Level 5
Calibration and System Performance Solution

Sample Analysis – The typical batch for sample analysis should include the following. Preparation of LCS, MS, MSD, and Duplicate sample extracts is described in the appropriate sample preparation SOP.

Tune Standard
Calibration and System Performance Solution
Instrument Blank
Method Blank
Laboratory Control Sample
Laboratory Control Sample Duplicate
20 samples
Matrix Spike
Matrix Spike Duplicate

Autosampler – Load the Autosampler with standards and samples for the batch created above.

12.10.1.4 Analyze Samples – Analyze all standards, quality control samples, and environmental samples.

12.10.1.5 Process all runs with Target software

12.10.1.6 View sample chromatograms and verify analyte identifications (Section 12.11).

12.10.1.7 Post data to EPIC Pro.

12.11. **Data Reduction**

12.11.1. Qualitative Analysis: This must be done on every sample and quality control standard.

12.11.1.1 **Retention Time Comparison:** The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of RT in the presence of co eluting components.

12.11.1.2 **Mass Spectrum Comparison:** The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met:

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.
- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.
- Additional client specific requirements for the analysis of contract samples requires all ions present in the reference mass spectrum at a relative intensity > 10% must be present in the sample spectrum.
- Due to limitations of the “Target” software, analyst discretion is advised.

Table 12.2 Primary and Secondary quantitation ions for target compounds[2]

Analyte	Primary Ion	Secondary Ions
Phenol	94	65, 66
Bis (2-Chloroethyl) ether	63	93, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
Benzyl Alcohol	108	79, 107
1,2-Dichlorobenzene	146	148, 111
2-Methylphenol	108	107, 79
Bis (2-Chloroisopropyl)ether	45	77, 121
3&4-Methylphenol	108	107, 79
N-Nitroso-di-n-propylamine	70	43, 101
Hexachloroethane	117	201, 199
1,4-Dioxane	88	58, 43
Benzaldehyde	105	106, 77
N-Nitrosodimethylamine	42	74
Aniline	93	66, 39
Acetophenone	105	77, 120
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	109, 65
2,4-Dimethylphenol	107	122, 121
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	128	129
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Caprolactam	55	56, 113
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	127, 164
2-Nitroaniline	65	92, 138
Dimethylphthalate	163	194, 164
Acenaphthylene	152	153
2,6-Dinitrotoluene	165	63, 89
3-Nitroaniline	138	108, 92
Acenaphthene	154	153, 152
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65,39
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 89
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	108, 92
1,2,4,5-Tetrachlorobenzene	216	214, 179
2,3,4,6-Tetrachlorophenol	232	131, 166
4,6-Dinitro-2-methylphenol	198	51, 105

Analyte	Primary Ion	Secondary Ions
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	283.7	142, 249
Atrazine	200	173, 58
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	176, 179
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 203
Benzidine	184	185, 92
Pyrene	202	200, 203
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
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
Indeno(1,2,3-cd)pyrene	276	138, 277
Dibenz(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
Carbazole	167	168,169

[2]The information in this table was taken from Method 8270C. Please refer to the method for additional compounds and their applicable ions.

Analyte	Primary Ion	Secondary Ions
Internal Standards		
1,4-Dichlorobenzene-d_4	152	150, 115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265
Surrogates		
2-Fluorophenol (acid)	112	64
Phenol-d_6 (acid)	99	71
Nitrobenzene-d_5 (BN)	82	128, 54
2-Fluorobiphenyl (BN)	172	171
2,4,6-Tribromophenol (acid)	329.8	331.8, 141
Terphenyl-d_{14} (BN)	244	122, 212

[2]The information in this table was taken from Method 8270C. Please refer to the method for additional compounds and their applicable ions.

12.11.2. Internal Standard Assignment List (from Method SW-846 8270C-Table 5): this section lists the internal standard compounds and all target compounds that are assigned to each internal for quantitation:

1,4-Dichlorobenzene – d4
Aniline
Benzyl alcohol
Bis (2-chloroethyl)ether
Bis(2-chloroisopropyl)ether
2-Chlorophenol
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
2-Fluorophenol (surrogate)
Hexachloroethane
2-Methylphenol
4-Methylphenol
N-Nitroso-dimethylamine
N-Nitroso-di-n-propylamine
Phenol
Phenol-d6 (surrogate)
1,4-Dioxane
Pyridine
2-Chlorophenol-d4 (advisory surrogate)
Benzaldehyde
1,2-Dichlorobenzene-d4 (advisory surrogate)

Naphthalene-d8
Acetophenone
Benzoic acid
Bis(2-chlorethoxy)methane
4-Chloroaniline
4-Chloro-3-methylphenol
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dimethylphenol
Hexachlorobutadiene
Isophorone
2-Methylnaphthalene
Naphthalene
Nitrobenzene
Nitrobenzene-d8 (surrogate)
2-Nitrophenol
1-Methylnaphthalene
1,2,4-Trichlorobenzene

Acenaphthene-d10
Acenaphthene
Acenaphthylene
1,2-Diphenylhydrazine
2-Chloronaphthalene
4-Chlorophenyl phenyl ether
Dibenzofuran
Diethyl phthalate
Dimethyl phthalate
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Fluorene
2-Fluorobiphenyl (surrogate)
Hexachlorocyclopentadiene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
4-Nitrophenol
Biphenyl
2,4,6-Tribromophenol (surrogate)
2,4,6-Trichlorophenol
2,4,5-Trichlorophenol
1,2,4,5-Tetrachlorobenzene

Phenanthrene-d10
Atrazine
Anthracene
4-Bromophenyl phenyl ether
Di-n-butyl phthalate
4,6-Dinitro-2-methylphenol
Carbazole
Fluoranthene
Hexachorobenzene
N-Nitroso-diphenylamine
Pentachlorophenol
Phenanthrene

Chrysene-d12
Benzidine
Benzo(a)anthracene
Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Chrysene
3,3'-Dichlorobenzidine
Pyrene
Terphenyl-d6 (surrogate)
Di-n-octylphthalate

Perylene-d12
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(a)pyrene
Dibenz(a,h)anthracene
Indeno(123,cd)pyrene

12.12. Quantitative Analysis- Quantitation is based on the integrated abundance of the target analyte's quantitation ion using the internal standard technique.

12.12.1. **Raw Data Results:** The GC/MS data system will calculate the concentration of each analyte as µg/L (or ng/mL). For water samples, no further calculations are necessary unless a dilution of the sample has been performed. If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

12.13. **Tentatively Identified Compounds (TICs)** – For some samples, identification may be desired for non-target compounds. A mass spectral library search may be conducted to attempt assignment of tentative identifications. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications.

12.13.1. Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum;

12.13.2. The relative intensities of the major ions should agree within ± 20%;

12.13.3. Molecular ions present in the reference spectrum should be present in the sample spectrum;

12.13.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds;

12.13.5. 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.

12.13.6. For additional information on the determination of TICs, please see SOP: S-ALL-O-038, *Processing of TICs for GCMS* (most current revision or replacement).

13. Quality Control

13.1. Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per 20 samples	Target analytes must be less than reporting limit.	Qualify results and/or re-extract associated samples. ***Exceptions:*** If sample ND, report sample without qualification; If sample result >10x MB detects, report sample with appropriate qualifier indicating blank contamination; If sample result <10x MB detects, and sample cannot be re-extracted, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	Method specified compounds: **Base Neutrals**: 1,2,4-Trichlorobenzene; Acenaphthene; 2,4-Dinitrotoluene; Pyrene; N-nitroso-di-n-propylamine; 1.4-Dichlorobenzene **Acids**: Pentachlorophenol; Phenol; 2-Chlorophenol; 4-Chloro-3-methylphenol; 4-Nitrophenol *OR (alternative)* 70 compound LCS Mix	One per batch of up to 20 samples	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to the TNI standard.	At analyst discretion, Re-analyze the LCS to verify failure; If LCS passes, review samples for potential injection problems; If problem persists, check spike solution; Re-extract samples where possible. ***Exceptions:*** If LCS recovery is > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. Also, if the MS/MSD meet QC requirements, they may be used as acceptable criteria for the LCS.
Matrix Spike (MS)	Method specified compounds: **Base Neutrals**: 1,2,4-Trichlorobenzene; Acenaphthene; 2,4-Dinitrotoluene; Pyrene; N-nitroso-di-n-propylamine; 1.4-Dichlorobenzene **Acids**: Pentachlorophenol; Phenol; 2-Chlorophenol; 4-Chloro-3-methylphenol; 4-Nitrophenol *OR (alternative)* 70 Compounds LCS Mix	One per batch of up to 20 samples EPA 625: One per batch of up to 10 samples	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to the TNI standard.	If LCS and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One for every 5% of all environmental samples EPA 625: One for every 10% of all environmental samples	Laboratory Derived Limits	Report results with an appropriate footnote.

13.2. **Table 13.2 – Sample Quality Control Criteria**

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	1,4-Dichlorobenzene-d4 Naphthalene-d8 Acenaphthene-d10 Phenanthrene-d10 Chrysene-d12 Perylene-d12	Added to all standards, samples, spikes, control samples, and method blanks prior to analysis	**Retention Time:** RT must be ± 30 seconds from last calibration check on all samples	**Retention Time Failure:** If matrix interference is NOT probable, the analytical system must be checked for source of retention time shifting; Affected samples should be reanalyzed in the absence of an obvious instrument or matrix related interference.
Surrogate Standards	Nitrobenzene-d5 2-Fluorobiphenyl Terphenyl-d14 Phenol-d6 2-Fluorophenol 2,4,6-Tribromophenol	Added to all samples, spikes, control samples and method blanks prior to analysis	Laboratory derived limits	1 Base neutral and 1 Acid surrogate are allowed to be outside of recovery limits before action is taken. Assess impact of sample matrix. In the absence of obvious matrix interference (high background, extremely dark extract), re-extract sample. ***Exceptions:*** Surrogate recovery above criteria and target compounds < RL, result may be reported with appropriate footnote. Surrogate recovery out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote.

14. Data Analysis and Calculations

14.1. **Results Calculation- Aqueous Samples:**

$$\text{Concentration } (\mu\text{g/L}) = \frac{(C_x)(V_x)(DF)}{(V_s)}$$

Where:

C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
V_s = Volume of water sample extracted (mL).

14.2. **Results Calculation- Soil/Solid Samples:**

$$\text{Concentration } (\mu\text{g/kg}) = \frac{(C_x)(V_x)(1000)(DF)}{(W_s)}$$

Where:

C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
W_s = Weight of soil sample extracted (g).

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Tables 11.2, 13.1, and 13.2.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Tables 11.2, 13.1, and 13.2

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Tables 11.2, 13.1, and 13.2.

18. Method Performance

18.1. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually per S-GB-Q-020, *Determination of LOD and LOQ* (most current revision or replacement) for each matrix per instrument.

18.2. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, Orientation and *Training Procedures*, (most current revision or replacement).

18.2.1. Analysis of four (4) replicates of reagent water spiked with 250µL of the 8270 LCS Spiking Solution and 10µL of nNPDA plus all other compounds that are currently reported at a concentration of 50µg/L or equivalent to the LCS. The recovery is to be within the current water LCS QC limits for the known concentrations and 30% RSD for all replicates.

18.2.2. Analysis of four (4) replicates of Ottawa sand spiked with 250µL of 8270C LCS Spiking Solution and 10µL of nNPDA plus all other compounds that are currently reported at a concentration of 1670µg/kg or equivalent to the LCS. The recovery is to be within the current LCS QC acceptance limits for the known concentration and 30% RSD for all replicates.

19. Method Modifications

19.1. Method modifications for EPA method 8270C are as follows:

- Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.
- All major modification to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.
- Procedures identified as “Best Practices” by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories.
- The laboratory follows the DFTPP Tune criteria outlined in EPA 525.2.
- The laboratory practice is to have thermal preservation at ≤6˚C. This is based on 40CFR Part 136, page 29808, footnote 18.
- If a client fails to provide the method required Matrix Spike/Matrix Spike Duplicate (MS/MSD), the laboratory will analyze a Laboratory Control Spike Duplicate to demonstrate precision. The analytical batch will be qualified with the “M5” data qualifier.

20. Instrument/Equipment Maintenance

20.1. Please refer to the instrument operations manual or the SOP S-GB-Q-008, *Preventative, Routine, and Non-routine Maintenance* (current revision or replacement).

21. Troubleshooting

21.1. Please refer to the instrument manufacturer operations manual.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

22.3. **Equipment:** Portions of the analytical instrumentation operate at high temperatures and under positive pressure. Care must be taken to minimize accidents and injuries when working on or with this equipment. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones. The GC pneumatic system uses gas under high pressure. This high pressure introduces the risk of injury due to flying glass and other objects should a vessel or line rupture. Safety glasses are highly recommended at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-GB-W-001, *Waste Handling and Management* (most current revision or replacement).

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. USEPA, SW-846, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), December 1996.

25.2. USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

25.3. USEPA, Method 625, Appendix A to Part 136, (1984), "Base/Neutrals and Acids".

25.4. USEPA, Method 525.2, Revision 2.0 (1995), "Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry".

25.5. Pace Quality Assurance Manual- most current version.

25.6. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.7. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: Client Specific Requirements.

26.2. Attachment II: Tailing Factor Calculation

27. Revisions

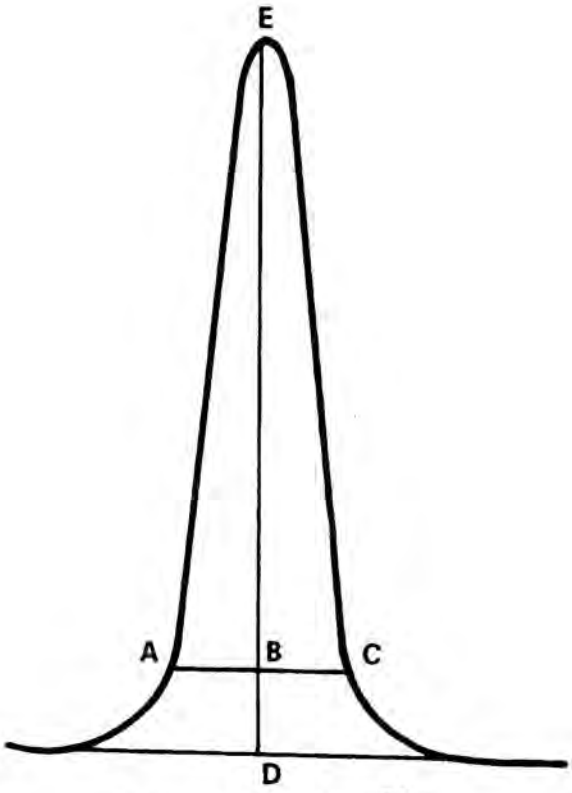
Document Number	Reason for Change	Date
S-GB-O-049-Rev.05	Throughout Document: Updated SOP format to be consistent with SOP: S-GB-Q-017 *Preparation of SOPs* Throughout Document: Renamed Tables to be consistent with current Section. Section 11.3: Changed ICV calculation criteria to match CCV calculation criteria. Table 11.Section 12.2.1: Updated DFTPP Tune Criteria to be consistent with EPA 525.2. Section 12.3: Added tailing factor criteria. Section 19: Added Modification in relation to tune criteria. Attachment II: Tailing Factor Calculation added.	30May2013
S-GB-O-049-Rev.06	Throughout Document: Updated laboratory name to Pace Analytical Services LLC – Green Bay WI Table 7.1: Updated temperature to ≤6˚C from 4±2˚C. Table 9.1 and 12.1: Updated information for 40MSS6/40MSS8, added 40MSSA. Table 9.2: Updated with current vendor information. Section 10.1: Added Acetone. Table 10.4: Changed standard and solvent amounts in calibration curve. Table 11.1: Added pyridine. Table 11.2: Updated SOP reference to most current revision. Table 11.3.1: Added CRDL language. Table 12.2: Updated 1˚ and 2˚ ions. Table 13: Updated MB criteria from 20X to 10X rule for qualification requirements. Section 22.1: Updated MSDS to SDS Section 23.1: Updated SOP reference	24Oct2016
S-GB-O-049-Rev.07	Section 12.11.1: Added to section that data reduction must be done on every sample and quality control standard.:	21Jun2017

Attachment I:

Throughout document, reference to Client Specific requirements refers to samples analyzed following: BP Technical Requirements LaMP Revision 10.1, Canadian National Railway Services and Technical Specifications Manual, GE Minimum Standards Revision 2.

Attachment II: DFTPP Tailing Factor Calculation

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)}$$



TAILING FACTOR= $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

Figure 13. Tailing factor calculation.

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STANDARD OPERATING PROCEDURE

DETERMINATION OF SEMI-VOLATILE ORGANICS BY GC/MS AND SIM (SELECTIVE ION MONITORING)

Reference Methods: EPA SW-846 Method 8270C SIM / EPA 625 SIM

Local SOP Number:	S-GB-O-050-Rev.04
Effective Date:	Date of Final Signature
Supersedes:	S-GB-O-050-Rev.03
SOP Template Number:	SOT-ALL-O-008-rev.01

APPROVALS

Nils Melberg, Laboratory General Manager — Date: 10/24/16

Kate Verbeten, Laboratory Quality Manager — Date: 10/24/16

Chris Haase, Laboratory Department Manager — Date: 09/16/16

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date

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TABLE OF CONTENTS

1. Purpose/Identification of Method

1.1. This Standard Operating Procedure (SOP) documents the procedures used by Pace Analytical Services, LLC – Green Bay WI to determine the concentration of Semi-volatile Organic Compounds in environmental samples using Selective Ion Monitoring (SIM). The laboratory utilizes GC/MS and bases these documented procedures on those listed in EPA SW-846 Method 8270C SIM and EPA 625. Samples for analysis are prepared by SW846 Method 3510C, SW846 Method 3540C and SW846 Method 3546 following Pace SOPs S-GB-O-053, *Separatory Funnel Extraction by SW846 3510C* (most current revision or replacement), and S-GB-O-045, *Extraction of Biological Samples for Base Neutral/Acids and PAH-SIM Analysis* and *Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons and Base/Neutral/Acid, and Total Petroleum Hydrocarbons s in Solid Matrices by SW846 3546* (most current revision or replacement).

2. Summary of Method

2.1. Sample extracts are prepared for analysis by an appropriate sample preparation method. The semivolatile organic compounds are introduced into the gas chromatograph (GC) by injecting an aliquot of the sample extract. The GC conditions are programmed to separate the analytes. The GC effluent is directly introduced to a mass spectrometer (MS) for both identification and quantification of analytes. Analytes are identified by comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected major (quantitation) ion relative to an internal standard using a multi-point calibration curve.

3. Scope and Application

3.1. This procedure is principally used to determine concentrations of polynuclear aromatic hydrocarbons (PAHs) but can also be used to determine concentrations of other neutral, acidic, and basic semi-volatile organic compounds in extracts prepared from many types of water samples, tissue, soil samples and wastes. Analytes must be soluble in dichloromethane and amenable to capillary gas chromatography. A list of applicable compounds is shown herein in Table 11.1. Pace Reporting Levels (PRLs) are also shown for water and soil samples. PRLs are subject to change based on current analytical system performance and actual sample matrices.

3.2. This method is applicable to most water and solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, tissue, sediment, soils, and other solid samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix related modifications must be documented within the analytical data.

3.3. This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of semi-volatile configured GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.4. This method cannot be substituted for other similar published methods where permit or regulatory compliance is required.

4. Applicable Matrices

4.1. This SOP applies to surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, tissue, soils, and sludges.

5. Limits of Detection and Quantitation

5.1. The reporting limit (LOQ) for all analytes is listed in Table 11.1 through 11.3 for the listed matrices. All current MDLs are listed in the LIMS and are available by request from the Quality Manager.

6. Interferences

6.1. Interferences may be introduced into sample extracts by contaminants in solvents, reagents, glassware, and any other material that comes in contact with the sample or extract during extract preparation. These interferences must be closely monitored by analyzing Method Blank samples and taking corrective action as required.

6.2. Matrix interferences may result from materials co-extracted from some samples.

6.3. Significant phthalate contamination may result at any time if consistent quality control is not practiced. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials.

6.4. Contamination by carryover can occur when high concentration extracts are analyzed prior to low concentration extracts. The contamination may also cause degradation of labile analytes. Whenever carryover is suspected, the affected extracts should be re-analyzed. If significant degradation of the GC/MS systems is suspected, system performances samples should be analyzed and corrective action taken as needed.

7. Sample Collection, Preservation, Shipment and Storage

7.1. **Table 7.1 – Sample Collection, Preservation, Storage, and Hold time**

Sample type	Collection per sample	Preservation	Storage	Hold time
LV PAH Aqueous	One 125mL amber glass	None	0-≤6°C	7 days
TCLP	One 1L amber glass	None	0-≤6°C	TCLP Leachates must be solvent extracted within 7 days of the completion of the tumbling process
Soil/Solid (non-aqueous)	One 8oz wide glass jar	None	0-≤6°C	14 days
Extracts	One 2mL glass vials, same as used for standard storage	None	≤ -10°C	40 days

8. Definitions

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary.

8.2. Run Sequence Log—A logbook that lists all injections and analyses performed on a particular piece of equipment regardless of the use of the data collected from each analysis.

8.3. Tune Period—The period after the DFTPP instrument tune check within which analyses may be performed.

9. Equipment and Supplies (Including Computer Hardware and Software)

9.1. **Table 9.1 - Instrumentation**

Equipment	Vendor	Model / Version	Description / Comments
Gas Chromatograph	HP	6890	40MSS2
Mass Selective Detector	HP	5973	40MSS2
Data System	HP	Chem Station	40MSS2
Auto-injector	HP	7683	40MSS2
Vacuum Pump (Rough)	HP	E2M2	40MSS2
Tray	HP	G2614A	40MSS2
Gas Chromatograph	HP	6890	40MSS4
Mass Selective Detector	HP	5973	40MSS4
Auto-injector	HP	7683	40MSS4
Tray	HP	G2614A	40MSS4
Vacuum Pump (Rough)	HP	G1099-80023	40MSS4
Data System	HP	Chem Station	40MSS4
Gas Chromatograph	Agilent	7890	40MSS7
Mass Selective Detector	HP	5975	40MSS7
Auto-injector	HP	7683B	40MSS7
Tray	HP	G2614A	40MSS7
Vacuum Pump (Rough)	HP	G1099-80023	40MSS7
Data System	HP	Chem Station. Gerstel Maestro	40MSS7
Gas Chromatograph	Agilent	6890N	40MSS9
Mass Selective Detector	HP	5975C	40MSS9
Auto-injector	HP	7683-G2613A	40MSS9
Tray	HP	G2614A	40MSS9
Vacuum Pump (Rough)	HP	G1099-80023	40MSS9
Data System	HP	Chem Station.	40MSS9

9.2. **Table 9.2 - Chromatography Supplies**

Item	Vendor	Model / ID	Catalog #	Description
Analytical Column	Restek	XTI-5 w/Integraguard	1223-124	30 m, 0.25 mm ID, 0.25 df
Fluorocarbon O-rings	Restek		20377	
Vespel/Graphite	Restek		20229	1/16” x0.4 mm ID
Gooseneck Splitless	Restek		20800	4 mm x 6.5 x 78.5 for
Guard Column	Restek		20231	0.5 MID
Ferrules	Fisher Scientific		5-5	
Analytical Column	Phenomenex	ZB-SV w/Integraguard	7HG-G027-11-GC	30m, 0.25mm ID, 0.25 df

9.3. **Table 9.3 - Glassware**

Glassware	Description	Vendor / Item # / Description
Volumetric Flasks	10mL, 25mL, 50mL	Class A
Glass Storage Vials	5mL, 10mL, 12mL, with Teflon-lined screw caps	MG Scientific/T102-3-INV, T102-1-I
Glass Autosampler Vials	2.0mL with Teflon-lined crimp or screw caps	MG Scientific/V300-3/V300-20N
Borosilicate Inserts	200µL low volume vial inserts	

9.4. **Table 9.4 - General Supplies**

Supply	Description	Vendor/ Item # / Description
Gas tight syringes	10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, and 1000-µL, as needed, Hamilton or equivalent.	Fisher Scientific/Various
Teflon dispensing bottles		
Pipettes	Borosilicate Glass 9” Pipette	MG Scientific/D200-9

10. Reagents and Standards

10.1. **Table 10.1 – Reagents and Stock Standards**

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Dichloromethane	MG Scientific, Burdick & Jackson	Pesticide Grade or equivalent
Acetone	Burdick & Jackson	Pesticide Grade or equivalent

10.2. Table 10.2 - Standard Definitions

Standard	Description	Comments
Tune Standard	Decafluorotriphenylphosphine (DFTPP), 4,4'-DDT, pentachlorophenol, and benzidine solution in dichloromethane used to verify ion response ratios and system inertness prior to analysis. [For PAH only analysis, breakdown and tailing factors do not need to be evaluated or controlled.]	Must inject no more than 50ng on column. The DFTPP must meet ion ratio criteria as per Section 12.2.1 [Some programs may not require that DFTPP meets ion ratio criteria. Labs must minimally analyze a DFTPP standard to verify mass axis alignment.]
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	Method requires a minimum of 5 levels
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	
Second Source Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the accuracy of the calibration curve.	
Internal Standard	A solution added to all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard is used to adjust response ratios to account for instrument drift.	Naphthalene-d_8 Acenaphthene-d_{10} Phenanthrene-d_{10} Chrysene-d_{12} Perylene-d_{12}
Surrogate Standard	A solution added to all samples, spikes, control samples, and method blanks prior to analysis.	2-Fluorobiphenyl Terphenyl-d_{14}
Spiking Standard	This solution contains all target analytes and should not be prepared from the same standards as the calibration standards.	

10.3. **Table 10.3 - Standard Storage Conditions**

Standard Type	Description	Expiration	Storage
Stock Solutions	▪ Concentrated reference solution purchased directly from approved vendor	▪ Manufacturer's recommended expiration date for unopened ampulated standards. ▪ Stock standards must be replaced 1 year after ampule is opened or on expiration date, whichever is sooner.	▪ Manufacturer's recommended storage conditions ▪ When standard is opened, record all information in the standard prep log program in Epic Pro.
Intermediate and Working Standard Solutions	▪ Reference solutions prepared by dilutions of the stock solution	▪ 1 year from preparation or the expiration date listed for the stock source, whichever is sooner. ▪ Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	▪ Store in amber vials with Teflon lined screw caps ▪ Stored at <-10, like sample extracts. If stock source conditions conflict, store according to method requirements.

10.4. **Standard Sources**: Standards are prepared from commercially available multi-compound stock solutions and neat materials by multiple dilutions. The sources of the stock solutions and neat materials, recipes for preparing dilutions and working standards, and concentrations for all compounds are presented in table 10.5. All intermediate standards are prepared using dichloromethane and stored in glass vials with Teflon lined caps or Mininert valves or as recommended by the standard manufacturer.

10.5. **Stock Standards:**

10.5.1. **Table 10.5 Stock Standards**

Standard	Conc.	Purity	Manufacturer	Vendor	Catalog #
DFTPP Tuning Standard	1000 µg/mL	99%	Supelco	Supelco	47548-4
Internal Standard	4000 µg/mL	99%	Restek	Restek	31006
Surrogate Standard	5000 µg/mL	99%	Restek	Restek	31082
Calibration Standard	500 µg/mL	99%	Accustandard	Accustandard	M-610-FL-R-5X
Calibration Standard	500 µg/mL	99%	O2SI	O2SI	114132-05-5pk
Benzo(e)pyrene Calibration Standard	1000 µg/mL	99%	Absolute Standard	Absolute Standard	71016
Initial Calibration Verification Standard	2000 µg/mL	99%	Supelco	Supelco	47543-U
Initial Calibration Verification Standard for Benzo(e)pyrene	50µg/mL	99%	Accustandard	Accustandard	H-112S

10.6. **Working Standard Preparation**: Working calibration standards are prepared in dichloromethane or a water soluble solvent. Standards made for direct analysis on the GC/MS are made in dichloromethane. Standards made for addition into samples as part of the preparation are made into acetone. Depending on the volume of each solution needed, the standards are brought to volume in volumetric flasks or prepared in smaller, glass vials and brought to volume by additions of solvent with micro syringes.

10.6.1. **Volumetric Flask Preparation** – Fill appropriate volumetric flask 2/3 full with dichloromethane/Acetone. Introduce appropriate amount of standard into dichloromethane/Acetone in flask with a micro-syringe. Dilute to volume with dichloromethane/Acetone.

10.7. **Calibration Standard Preparation**: Calibration standards are made into dichloromethane for the purpose of direct analysis by the analytical instrumentation. The standards must be made in a volumetric fashion. Several alternatives exist but the method employed by Pace – Green Bay utilizes volumetric flasks according to the following procedure.

10.7.1. Standards are prepared from commercially available multi-component stock solutions. The sources of materials, recipes for preparing dilutions and working standards, and concentrations for all compounds are presented below. All standards are prepared using dichloromethane and stored in amber vials with PTFE lined caps.

10.7.2. Storage and Stability of Analytical Standards –All standards must be stored in the dark at less than -10°C or at a temperature recommended by the manufacturer. They must be replaced every 12 months or sooner if the standards show signs of degradation. As each standard, from the vendor is opened, record all pertinent information in the electronic standards logbook in Epic Pro. Record all standard preparations in the standard logbook.

10.8. **Preparation Procedures**

10.8.1. **DFTPP Tuning Solution:**

10.8.1.1 **Soil Analysis**: A Dichloromethane solution containing 50ng/µL of decafluorotriphenylphosphine (DFTPP) is prepared. A stock solution; Supelco cat.# 47548-4; containing DFTPP at 1000µg/mL, is diluted taking 1.25mL and diluting to 25mL of dichloromethane.

10.8.1.2 **Aqueous Analysis**: Since the aqueous analysis requires a 2ul injection, A Dichloromethane solution containing 25ng/µL of decafluorotriphenylphosphine (DFTPP) is prepared. The Soil and Aqueous Intermediate Tune Solution from Section 10.7.1.1; containing DFTPP at 50µg/mL, is diluted taking 500µL and diluting to 1mL of dichloromethane.

10.8.2. **Internal Standard Solutions:**

10.8.2.1 **Stock Solution** – Obtained from Restek cat. #31006 containing 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12 and Perylene-d12 all at 4000µg/mL in dichloromethane.

10.8.2.1.1 **Water Intermediate Standard -** This intermediate standard is prepared by diluting 50µL up to 10mL of dichloromethane, producing a solution that is 20µg/mL for each component. 10µL of this standard is added to 1mL of every standard, sample, spike and blank analyzed by this method. Producing an on-column concentration of 200µg/L.

10.8.2.1.2 **Soil Intermediate Standard -** This intermediate standard is prepared by diluting 500µL up to 1.0mL of dichloromethane, producing a solution that is 2000 µg/mL for each component. 10µL of this standard is added to 1mL of every standard, sample, spike and blank analyzed by this method. Producing an on column concentration of 20µg/mL.

10.8.3. **Surrogate Standard Solution:**

10.8.3.1 **Water Working Standard**: Water Stock surrogate Solution obtained from Restek, cat. #31082 containing 1,2-Dichlorobenzene-d4, Nitrobenzene-d5, 2-Fluorobiphenyl and p-Terphenyl-d14 all at 1000µg/mL in dichloromethane. The working standard is prepared by diluting 1.0mL up to 500mL of acetone, producing a standard that is 0.2µg/mL of each component. 100ul of this working standard is spiked into all QC and Samples, producing and on-column value of 200µg/L.

10.8.3.2 **Soil Working Standard**: Soil Stock Solution obtained from Restek. Cat #31082 containing 1,2-Dichlorobenzene-d4, Nitrobenzene-d5, 2-Fluorobiphenyl and p-Terphenyl-d14 all at 5000µg/mL in dichloromethane. The working standard is prepared by diluting 3000µL up to 100mL of acetone, producing a standard that is 150µg/mL of each component. 100µL of this working standard is spiked into all QC and Samples, producing and on-column value of 15µg/mL.

10.8.4. **Laboratory Control Spike/Matrix Spike/Duplicate Solution:**

10.8.4.1 **Water LCS/MS Standard**: Water Stock solution is obtained from Accustandard, product # M-610-FL-R-5X, containing the 18 PAH compounds, all at 500µg/mL. Intermediate standard is prepared by diluting 400µL of the 500µg/mL up to 100mL with Acetone. 100uL of this standard is spiked into all Lab Control and Matrix Spikes, producing an on-column concentration of 200µg/L.

10.8.4.2 **Soil Standard**: Stock solution is obtained from O2SI, product # 114132-05-5pk, containing the 18 PAH compounds, all at 500µg/mL. 20 µL of this solution is spiked into all LCS and MS samples, producing an on-column concentration of 10µg/mL.

10.8.5. **Initial Calibration Intermediate Standard**

10.8.5.1 **Water Samples:** Stock solution is obtained from O2SI, product #114132-05-5pk, containing the 18 PAH compounds, all at 500µg/mL. The intermediate is prepared by diluting 40µL of the 500µg/L PAH stock along with 20µL of the Water Stock surrogate Solution obtained from Restek, cat. #31082 containing 1,2-Dichlorobenzene-d4, Nitrobenzene-d5, 2-Fluorobiphenyl and p-Terphenyl-d14 all at 1000µg/mL in dichloromethane up to 10.0mL dichloromethane, producing an intermediate calibration standard that is 2000µg/L of all components.

10.8.5.2 **Soil Samples:** Stock solution is obtained from O2SI, product #114132-05-5pk, containing the 18 PAH compounds, all at 500µg/mL , containing the 18 PAH compounds, all at 500µg/mL. The intermediate is prepared by diluting 1250 µL of the 500 µg/mL PAH Stock Standard along with 125 µL of the 5000 µg/mL B/N Surrogate Stock Solution to 25.0 mL with methylene chloride producing the high standard of 25 µg/mL. Per Client Request Benzo(e)pyrene may be included as a separate calibration curve. Stock Solution is obtained from Absolute Standards, catalog # 71016, containing Benzo(e)pyrene at 1000µg/mL. The intermediate is prepared by diluting 250µL of 1000µg/mL Benzo(e)pyrene Stock Standard up to 10.0mL dichloromethane, producing an intermediate calibration standard that is 25µg/mL. The standards are then further diluted to obtain the concentrations used for calibration.

10.8.6. **Initial Calibration Working Standards:**

10.8.6.1 **Water Initial Calibration Curve**: The following working calibration standards are prepared by using the Initial Calibration Intermediate Standard for Water Samples listed above (10.8.5.1):

Standard Concentration ug/mL	Amount of Intermediate Standard Added (µL)	Amount of Intermediate Internal Standard Added (µL)	Final Volume (µL)
0.005	2.5	10	1010
0.025	12.5	10	1010
0.050	25	10	1010
0.100	50	10	1010
0.200	100	10	1010
0.500	250	10	1010
1.000	500	10	1010
2.000	1000	10	1010
CCV - .200	100	10	1010

10.8.6.2 **Soil Initial Calibration Curve**: The following working calibration standards are prepared by using the Initial Calibration Intermediate Standard for Soil Samples listed above (10.8.5.2):

Standard Concentration ug/mL	Amount of Intermediate Standard Added (µL)	Amount of Intermediate Internal Standard Added (µL)	Final Volume (µL)
0.25	10	10	1010
0.50	20	10	1010
1.0	40	10	1010
4.0	160	10	1010
10.0	400	10	1010
20.0	800	10	1010
25.0	1000	10	1010
CCV – 10.0	400	10	1010

10.8.7. **Initial Calibration Verification Standards:**

10.8.7.1 **Water Initial Calibration Verification Standard:** Stock Solution is obtained from Supelco, cat# 47543-U, containing the 18 PAH compounds all at 2000µg/mL. A working solution is prepared by diluting 5µL of the 2000µg/mL PAH stock, along with 10µL of the Water Stock surrogate Solution obtained from Restek, cat. #31082 containing 1,2-Dichlorobenzene-d4, Nitrobenzene-d5, 2-Fluorobiphenyl and p-Terphenyl-d14 all at 1000µg/mL in dichloromethane up to 50mL with dichloromethane. This produces an ICV with a concentration of 200µg/L.

10.8.7.2 **Soil Initial Calibration Verification Standard:** Stock solution is obtained from Supelco, cat # 47543-U, containing the 18 PAH compounds, all at 2000 µg/mL. An intermediate is prepared by diluting 100 µL of the 2000 µg/mL PAH Stock along with 40 µL of 5000 µg/mL B/N Surrogate Stock Solution to 2.0 mL with dichloromethane. To produce the working ICV solution, the above intermediate ICV solution is further diluted by taking 100 µL of the intermediate ICV and diluting to 1.0 mL with dichloromethane to produce a 10 µg/mL working ICV standard. A separate Benzo(e)pyrene ICV is required. Stock Solution is obtained from Accustandard, catalog # H-112S, containing Benzo(e)pyrene at 50µg/mL. The working ICV solution is prepared by diluting 200µL of 50µg/mL Benzo(e)pyrene Stock Standard up to 1.0mL dichloromethane to produce a working initial calibration verification standard that is 10µg/L.

11. Calibration and Standardization

11.1. **Tune Verification –** The mass spectrometer tune status must be verified prior to initial calibration and at the beginning of each analytical sequence. For analysis by Selective Ion Monitoring, the response ratio criteria for DFTPP may be immaterial unless a custom spectral library were established under SIM conditions. Therefore, unless a program specific requirement mandates ion ratio criteria be followed, the laboratory must analyze a DFTPP standard but only for the purpose of verifying the alignment of the mass spectral axis. If the quality program requires otherwise and the ion ratios do not meet the criteria for the method, follow the equipment manufacturers' instructions for re-tuning the mass spectrometer. The tune status must be verified after the tuning procedures.

11.2. **Initial Calibration:**

11.2.1. **Analysis of Standards**: An initial calibration curve using a minimum of five points is analyzed prior to analyzing client samples. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values. Refer to table 11.1 for compound concentrations.

Table 11.1: Calibration standard compound concentrations for Water Analysis

Analyte	PQL water (µg/L)	Std 1 µg/mL	Std 2 µg/mL	Std 3 µg/mL	Std 4 µg/mL	Std 5 µg/mL	Std 6 µg/mL	Std 7 µg/mL	Std 8 ug/mL
Acenaphthene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Acenaphthylene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Anthracene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Benz(a)anthracene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Benzo(a)pyrene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Benzo(b)fluoranthene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Benzo(g,h,i)perylene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Benzo(k)fluoranthene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Chrysene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Dibenz(a,h)anthracene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Fluoranthene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Fluorene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Indeno(1,2,3-cd)pyrene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
2-Methylnaphthalene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Naphthalene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Phenanthrene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
Pyrene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0
1-Methylnaphthalene	0.0050	0.005	0.025	0.050	0.100	0.200	0.500	1.0	2.0

Table 11.2: Calibration standard compound concentrations for Soil Analysis

Analyte	PQL soil (µg/kg)	Std 1 µg/mL	Std 2 µg/mL	Std 3 µg/mL	Std 4 µg/mL	Std 5 µg/mL	Std 6 µg/mL	Std 7 µg/mL
Acenaphthene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Acenaphthylene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Anthracene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Benz(a)anthracene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Benzo(a)pyrene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Benzo(b)fluoranthene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Benzo(g,h,i)perylene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Benzo(k)fluoranthene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Chrysene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Dibenz(a,h)anthracene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Fluoranthene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Fluorene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Indeno(1,2,3-cd)pyrene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
2-Methylnaphthalene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Naphthalene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Phenanthrene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
Pyrene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0
1-Methylnaphthalene	16.7	0.25	0.50	1.0	4.0	10.0	20.0	25.0

11.2.2. Calibration Response Factors: Response factors (RF) establish the relationship of the instruments response in comparison with the concentration of any given analyte. The RF includes the concentration and response of the internal standard as well. By relating the IS concentration and response in an inverse manner, the target analyte concentration is adjusted to account for drift in the instrument on a per injection basis. As instrument response increases as indicated by the response of the internal standard, the concentration of the target is mathematically decreased, and vice versa.

11.2.3. To calculate the RF for any given calibration standard (or calibration verification standard), tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation:

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

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_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L).

11.2.4. Most, if not all modern chromatography data systems are capable of calculating this factor and using it to quantify analyte concentrations. The 8270C method has minimum requirements that these response factors must meet in order to be considered valid. The method uses a subset of the target analyte list to evaluate the performance of the system. These compounds are referred to as the System Performance Check Compounds or the SPCCs. The SPCCs serve as an indicator of instrument sensitivity and, by meeting a minimum value, ensure that the laboratory has adequate sensitivity to analyze and reliably report data for environmental samples. For the SIM method, all target compounds are considered to be SPCC compounds and the average RF for each SPCC compound must be as follows:

Naphthalene	≥0.700
2-Methylnaphthalene	≥0.400
Acenaphthylene	≥0.900
Acenaphthene	≥0.900
Fluorene	≥0.900
Phenanthrene	≥0.700
Anthracene	≥0.700
Fluoranthene	≥0.600
Pyrene	≥0.600
Benzo(a)anthracene	≥0.800
Chrysene	≥0.700
Benzo(b)fluoranthene	≥0.700
Benzo(k)fluoranthene	≥0.700
Benzo(a)pyrene	≥0.700
Benzo(e)pyrene	≥0.700
Indeno(1,2,3-cd)pyrene	≥0.500
Dibenz(a,h)anthracene	≥0.400
Benzo(g,h,i)perylene	≥0.500

Two of the PAH's response factors are allowed to not meet these requirements.

11.2.5. **Calibration Curve Fit**: The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. The curve is produced in several ways depending on the nature of the "goodness of fit".

11.2.6. **Average Response Factor (ARF)**: The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. It is in the most basic sense, a linear regression that is forced through zero at the origin. Because of its simplicity and the interception of the y axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of the ARF:

$$\%RSD = SD*100 / ARF$$

Where: SD = Standard deviation of the averaged RFs for a given compound

11.2.7. The average response factor is also used to diagnose the integrity of the chromatography system as it relates to calibration linearity. The ***Calibration Check Compounds (CCCs)*** are a subset of the target analyte list that must meet specific criteria for the calibration to be acceptable. For the CCCs, the %RSD for each is compared to the method criteria (≤ 30% for CCCs). If that of any CCC exceeds the criteria, the system needs to be inspected for potential sources of errors and recalibrated. **For the SIM method, all target compounds are considered CCC compounds.**

11.2.8. **Linear Regression**: The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y=ax+b where "a" is the slope of the line and "b" is the y intercept. In order to use this curve fit technique, a minimum of 5 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument is linear in nature but does not necessarily intercept the y axis at the origin. However, because the linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve.

11.2.9. **Non-linear Regression**: The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument gradually decreases with increasing concentrations. Using this technique, an analyst may be able to generate calibration curves with correlation coefficients very close or equivalent to 1.000. However, because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. Likewise, high levels of contamination may not be able to be calculated due to regression equations with multiple intercepts of either axis on the calibration plot.

11.2.10. A calculation of the coefficient of determination (COD) is used to determine the acceptability of a non-linear regressed curve. Either the low or high calibration points may be dropped to meet linearity criteria provided the laboratory meets the minimum 5 calibration point requirements. Points within the center of the curve may not be dropped unless an obvious problem is discovered and documented. The point must be dropped in its entirety and reanalyzed. Re-analysis should be within the same 12 hour time window and must occur within 8 hours of the original analysis.

11.3. **Calibration Verification**:

11.3.1. Low Level Calibration Check(CRDL): The lowest range of the calibration will be checked by either refitting the lowest calibration point against the calibration curve or re-analyzing the lowest calibration point. The CRDL must be checked before running any sample from MN and must meet a recovery of 60-140% of the expected value. Any compounds failing must be flagged in MN samples as failing to meet CRDL limits.

11.3.2. **Second Source Verification**: In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

11.3.3. Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\%\ Difference = \frac{(RFccv - AveRFcal)}{AveRFcal} * 100$$

$$\%\ Drift = \frac{(Result\ CCV - True\ Value\ CCV)}{True\ Value\ CCV} * 100$$

11.3.4. **Continuing Calibration Verification (CCV)**: As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***. The validity of the initial calibration is checked at the beginning of every analytical sequence and every 12 hours thereafter for as long as the instrument is analyzing samples and is accomplished by analyzing a midpoint calibration standard (CCV).

11.3.5. The values obtained from the analysis of the CCV are compared to the true values and a percent change calculated. The percent change must meet the method specified criteria for the analysis to proceed for an additional 12 hours.

11.3.6. The actual determination of change in instrument response is based on the type of curve fit used for each analyte. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the CCV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

$$\%\ Difference = \frac{(RFccv - AveRFcal)}{AveRFcal} * 100$$

$$\%\ Drift = \frac{(Result\ CCV - True\ Value\ CCV)}{True\ Value\ CCV} * 100$$

Table 11.4: Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Response Factor	%RSD ≤ 15%	If not met, try linear regression fit
	Linear Regression	r ≥ 0.99	If not met, try non-linear regression fit
	Non-linear Regression	COD ≥ 0.99	If not met, remake standards and recalibrate
System Performance Check Compounds (SPCCs)	All target compounds	Naphthalene ≥0.700 2-Methylnaphthalene ≥0.400 Acenaphthylene ≥0.900 Acenaphthene ≥0.900 Fluorene ≥0.900 Phenanthrene ≥0.700 Anthracene ≥0.700 Fluoranthene ≥0.600 Pyrene ≥0.600 Benzo(a)anthracene≥0.800 Chrysene ≥0.700 Benzo(b)fluoranthene ≥0.700 Benzo(k)fluoranthene ≥0.700 Benzo(a)pyrene ≥0.700 Benzo(e)pyrene ≥0.700 Indeno(1,2,3-cd)pyrene ≥0.500 Dibenz(a,h)anthracene ≥0.400 Benzo(g,h,i)perylene ≥0.500 Two of the PAH's response factors are allowed to not meet these requirements.	Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, poor purging efficiency, and active sites in the column or chromatographic system. Additional client specific requirements for the analysis of contract samples requires that all PAH's and surrogate compounds also be considered SPCCs and must meet the minimum RRF criterion of 0.05.
Calibration Check Compounds (CCCs)	All target compounds	%RSD < 30%	%RSD for the calibration check compounds (CCC's) must be ≤30% regardless of curve fit used.
Second Source Verification Standard	Immediately after each initial calibration	% Drift ±30% % Diff ±30% When used as a CCV for the reporting of sample data %Drift/Diff must meet CCV criteria.	Acceptance criteria are ±30% for all analytes. Additional client specific requirements for the analysis of contract samples requires that all compounds must be within ±20%
Continuing Calibration Verification	Prior to the analysis of any samples and every 12 hours thereafter		If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back without performing some maintenance.
	SPCCs	Must meet response criteria listed above	
	Internal Standard RT	RT ± 30 sec	Use midpoint calibration standard as reference
	Internal Standard Response	50 – 200%	Use midpoint calibration standard as reference
	CCCs	RF ± 20% Diff. Result ± 20% Drift	Use for Avg RF calibration curves Use for linear and non-linear calibration curves

11.4. **Calibration Corrective Actions:**

11.4.1. Calibration Linearity Problems:

11.4.1.1 Check instrumentation/equipment condition. Document instrument maintenance in the logbook.

11.4.1.2 Perform another initial calibration.

11.4.1.3 No data can be reported

11.4.1.4 Generate a Non-Conformance Memo.

11.4.2. Second Source Verification Problems:

11.4.2.1 Reanalyze the original ICV standard to determine instrument consistency.

11.4.2.2 Prepare and analyze a new ICV standard to determine preparation consistency/standard integrity.

11.4.2.3 Check instrumentation/equipment condition. Document instrument maintenance in the logbook.

11.4.2.4 Reanalyze ICV standard to determine if maintenance was effective in restoring performance. If the second ICV is acceptable, the analytical sequence is continued. If both ICVs fail, the analytical sequence is terminated and corrective action is initiated.

11.4.2.5 Perform another initial calibration.

11.4.2.6 No data can be reported.

11.4.2.7 Generate a Non-Conformance Memo.

11.4.3. Continuing Calibration Verification Problems:

11.4.3.1 Reanalyze the original CCV standard to determine instrument consistency.

11.4.3.2 Prepare and analyze a new CCV standard to determine preparation consistency/standard integrity.

11.4.3.3 Document instrument maintenance.

11.4.3.4 Reanalyze CCV standard to determine if maintenance was effective in restoring performance. If the second CCV is acceptable, the analytical sequence is continued. If both CCVs fail, the analytical sequence is terminated and corrective action is initiated.

11.4.3.5 Complete recalibration of instrument.

11.4.3.6 If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

11.4.3.7 *Exceptions:* If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis.

11.4.4. General Comment: When constructing a initial calibration curve, the analyst can drop curve points as follows:

11.4.4.1 The lowest curve point can be dropped as long as there is a standard that can meet the necessary reporting limits of the associated samples (or the reporting limits would have to be raised accordingly).

11.4.4.2 The highest curve point, or points, can be dropped but this decreases the upper calibration range, thereby limiting the analyst to reporting data within this new calibration range (this may cause more dilutions).

11.4.4.3 Mid-point injections in the curve can be removed if it can be proven that it was a bad injection, instrument failure, etc. The same curve point is required to be reanalyzed and incorporated in the curve prior to sample analysis. A supervisor or the Quality Manager is required to approve any such instance.

12. Procedure

12.1. **Operating Parameters:** Configure the GC/MS system to match the following operating parameters based on instrument configuration. The parameters themselves are saved as a method on the chromatography data system. By loading the last method used, the instrument will auto-configure to match the parameters from the last time the system was operated under that method. Verify that the settings in the software match the appropriate configuration.

Table 12.1: Instruments and Operating Parameters

Instrument IDs	Component	Settings and Consumables	
40MSS2	Gas Chromatograph	Column: Restek XTI-5 w/ Integraguard 30m, 0.25mm ID, 0.25df Inlet Liner: Restek 4 mm Single Gooseneck Injection Port Liners w/glass wool Inlet Seal: Restek Dual vespel ring stainless inlet seal Column Ferrules: Restek 0.4mm Vespel/Graphite	**Pressure / Flow: 2.0mL/min** **Initial Temperature: 100°C** **Initial Time: 1.5 min** **Fi**nal Temperature: 60°C/min to 155°C 20°C/min to 320°C 3 min hold Final Time: 13.67 min Injector Temperature: 295°C Detector Temperature: 310 Mode: Pulsed Splitless Pressure 20.969 psi Injection Pulse pressure 100psi for 1min
	Mass Spectrometer	Tune File: Named to date of tune	
	Autosampler	1.0 µL Injection 3 Solvent rinses from each solvent vial	
Instrument IDs	**Component**	**Settings and Consumables**	
40MSS4	Gas Chromatograph	Column: Phenomenex ZB-Semivolatiles w/ Guard 30m, 0.25mm ID, 0.25df Inlet Liner: Restek 4 mm Single Gooseneck Injection Port Liners w/glass wool Inlet Seal: Restek Dual vespel ring stainless inlet seal Column Ferrules: Restek 0.4mm Vespel/Graphite	Pressure / Flow: 2.0mL/min Initial Temperature: 100°C Initial Time: 1.5 min Final Temperature: 60°C/min to 155°C 20°C/min to 320°C 3 min hold Final Time: 13.67 min Injector Temperature: 295°C Detector Temperature: 310 Mode: Pulsed Splitless Pressure 20.969 psi Injection Pulse pressure 100psi for 1min
	Mass Spectrometer	Tune File: Named to date of tune	
	Autosampler	1.0 µL Injection 3 Solvent rinses from each solvent vial	

Instrument IDs	Component	Settings and Consumables	
40MSS7	Gas Chromatograph	Column: Phenomenex ZB-Semivolatiles w/ Guard 30m, 0.25mm ID, 0.25df Inlet Liner: Restek 4 mm Single Gooseneck Injection Port Liners w/glass wool Inlet Seal: Restek Dual vespel ring stainless inlet seal Column Fe**rrules: Restek 0.4mm Vespel/Graphite** Inlet Liner:	Mode: Pulsed Split Pressure 20.969 psi Injection Pulse pressure 100psi for 1min Pressure / Flow: 2.0mL/min Initial Temperature: 100°C Initial Time: 1.5 min Final Temperature: 60°C/min to 155°C 20°C/min to 320°C 3 min hold Final Time: 13.67 min Injector Temperature: 300°C Detector Temperature: 300 C
	Mass Spectrometer	Tune File: Named to date of tune	
	Autosampler	2.0 µL Injection 3 Solvent rinses from each solvent vial	
Instrument IDs	**Component**	**Settings and Consumables**	
40MSS9	Gas Chromatograph	Column: Restek XTI-5 w/ Phenomenex ZB-Semivolatiles w/ Guard 30m, 0.25mm ID, 0.25df Inlet Liner: Restek 4 mm Single Gooseneck Injection Port Liners w/glass wool Inlet Seal: Restek Dual vespel ring stainless inlet seal Column Fe**rrules: Restek 0.4mm Vespel/Graphite**	Pressure / Flow: 2.0mL/min Initial Temperature: 100°C Initial Time: 1.5 min Final Temperature: 60°C/min to 155°C 20°C/min to 320°C 3 min hold Final Time: 13.67 min Injector Temperature: 300°C Detector Temperature: 310 Mode: Pulsed Split Pressure 20.969 psi Injection Pulse pressure 100psi for 1min
	Mass Spectrometer	Tune File: Named to date of tune	
	Autosampler	2.0 µL Injection 3 Solvent rinses from each solvent vial	

12.2. **Tune Verification**: At the beginning of each analytical sequence, prior to the analysis of any standards or samples, the mass spectrometer tune conditions must be verified. This is done by analyzing a standard containing DFTPP (refer to table 12.2). The tune verification standard can be combined with the CCV standard provided that the amount of DFTPP introduced into the system meets the method criteria. For semi-volatile analysis, the system must also be verified for inertness **unless PAHs are the only class of analytes to be analyzed**. This is done simultaneously by the inclusion of DDT, benzidine and pentachlorophenol. DDT is used to verify breakdown conditions; benzidine and pentachlorophenol are used to check for tailing due to system activity.

12.2.1. Mass Axis Alignment / Ion Ration Verification

After the analysis of this standard, the mass spectrum of DFTPP must be evaluated against the following criteria:

Table 12.2: Tune Evaluation Criteria

Mass (m/z)	Mass Axis criteria	Ion Abundance criteria
51	Present	10.0-80.0% of m/z 198
68		<2.0% of m/z 69
69	Present	Present
70		<2.0% of m/z 69
127	Present	10.0-80.0% of m/z 198
197		<2.0% of m/z 198
198	Present	Base peak, >50% of Mass 442
199	Present	5.0-9.0% of m/z 198
275	Present	10.0-60.0% of m/z 198
365		>1% of m/z 198
441		Present, but less than m/z 443
442	Present	>50% of m/z 198
443	Present	15.0-24.0% of m/z 442

12.2.2. To evaluate the tune spectra, following the operating instructions for the chromatography data system to access the data file and obtain mass spectra for DFTPP. If the software has a program or macro for automatically selecting the spectra and evaluating the response ratios, use this option. Otherwise, the spectra must be obtained in one the following manners, in the listed order:

12.2.2.1 Using an average of three scans, centered on the apex of the peak; or,

12.2.2.2 Using an average of all scans across the width of the peak, taken at half height; or,

12.2.2.3 Using an average of all scans taken across the width of the peak from baseline to baseline.

A background scan taken immediately before but not including the peak must be subtracted.

12.2.3. Once obtained, evaluate the ion ratios against the criteria listed above. If the ratios meet the criteria, then analysis may proceed for 12 hours. The window for analysis is 12 hours from the injection date / time for the DFTPP tune verification. After that, the tune must be verified again to establish a new analytical window. The same Ion Abundance Criteria used for the DFTPP tune coupled with the initial calibration must be used for all subsequent analyses associated with that initial calibration.

12.2.4. If the ratios do not meet the criteria, refer to the following corrective actions to address the problem:

12.2.4.1 If the tune standard does not meet the criteria, refer to the following corrective actions to address the problem.

12.2.4.1.1 Retune the mass spectrometer following the equipment manufacturers' instructions. The tune status must be verified after the tuning procedures.

12.2.4.1.2 If this fails, change filament and retune.

12.2.4.1.3 If this fails, take down the mass spectrometer and clean the instrument.

12.3. **Calibration Verification**: After the instrument tune conditions are verified and the system meets tune criteria, the instrument must undergo calibration verification. If it has already been determined that the instrument needs to be recalibrated, follow the procedures listed in section 11.2.1 (Analysis of Standards). Otherwise, analyze a Continuing Calibration Verification Standard to determine the current calibration status.

12.4. If the CCV meets control criteria, the system is deemed to be in control and analysis of samples may commence. If the CCV does not meet control criteria, follow the corrective action procedures listed section 11.4.3 (Continuing Verification Problems). If the tune verification has been combined with the CCV, the 12 hour analysis window begins from the analysis date / time of the CCV.

12.5. *Note:* In situations where the instrument will run unattended (i.e. overnight), the analyst may load sequential CCVs in anticipation of that the first in the series may fail due to carry over from a previous sample. If so, the CCV must be evaluated according to the protocol set forth in the Quality Assurance Manual within the Equipment and Measurement Traceability section.

12.6. **Sample Preparation- Water Samples**: Aqueous samples are prepared according to EPA 3510C. These procedures are contained in a separate standard operating procedure. Refer to SOP number S-GB-O-053, *Separatory Funnel Extraction by 3510C* (most current revision or replacement) for details on the preparation of aqueous samples.

12.6.1. Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10µL of the internal standard solution.

12.7. **Sample Preparation- Soil Samples**: Aqueous samples are prepared according to EPA 3546. These procedures are contained in a separate standard operating procedure. Refer to SOP number S-GB-O-045 *Microwave Extraction for the Determination of Polynuclear Aromatic Hydrocarbons, Base/Neutral/Acids, and Total Petroleum Hydrocarbons in Solid Matrices by 3546* (most current revision or replacement) for details on the preparation of soil or solid samples.

12.7.1. Prior to analysis, each sample, MB, LCS, MS, and MSD is spiked with 10µL of the internal standard solution.

12.8. **Dilutions**

12.8.1. Dilutions on sample extracts must be prepared in a volumetric fashion. Sample aliquots should be taken in volumetric syringes and brought to volume by the addition of solvent via an appropriate syringe. In the event a dilution is made to bring a target analyte into calibration range, the analyst should make a dilution such that the target analyte is roughly the equivalent of the mid calibration point whenever possible. If dilutions are made on extracts that already contain internal standards, a proportional aliquot of internal standard solution must be added to the diluted extract based on the volume of diluent used.

12.9. **Sample Analysis-**

12.9.1. GC/MS System Preparation

12.9.1.1 Operating Parameters—Set up the instrument parameters shown in Table 12.1.

12.9.1.2 System Tuning and GC Performance Checks—Analyze the Tuning Solution and tune the mass spectrometer to meet the criteria shown in Section12.2.2. Verify acceptable GC system performance is described in Section 12.2.2. Print out a tune report.

12.9.2. Batch Sequence—Generate a sequence to run a batch of samples.

12.9.2.1 Initial Calibration – The typical batch for initial calibration should include:

Tune Standard
Calibration Level 1
Calibration Level 2
Calibration Level 3
Calibration Level 4
Calibration Level 5
Calibration and System Performance Solution

12.9.2.2 Sample Analysis – They typical batch for sample analysis should include the following. Preparation LCS, MS, MSD, and Duplicate sample extracts is described in the appropriate sample preparation SOP.

Tune Standard
Calibration and System Performance Solution
Instrument Blank
Method Blank
Laboratory Control Sample
Laboratory Control Sample Duplicate
20 samples
Matrix Spike
Matrix Spike Duplicate

12.9.3. Autosampler – Load the autosampler with standards and samples for the batch created above.

12.9.4. Analyze Samples – Analyze all standards, quality control samples, and environmental samples.

12.10. Qualitative Analysis

12.10.1. **Retention Time Comparison:** The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of RT in the presence of co eluting components.

12.10.2. **Mass Spectrum Comparison:** The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met:

12.12.2.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.

12.12.2.2. The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

12.12.2.3. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.

12.12.2.4. Under SIM conditions, only those ions collected will be present in the spectrum. Therefore, the best benchmark for spectral comparison should be the spectra obtained from

the opening CCV. Ion intensity ratios should agree within 30% of those obtained in the standard.

12.12.3. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

Table 12.3: Ions

Compound	CAS Number	Primary Ion	Secondary Ion
Naphthalene	91-20-3	128	129
2-Methylnaphthalene	91-57-6	142	141
1-Methylnaphthalene	90-12-0	142	141
Acenaphthylene	208-96-8	152	153
Acenaphthene	83-32-9	154	152
Fluorene	96-73-7	166	165
Phenanthrene	85-01-8	178	179
Anthracene	120-12-7	178	176
Fluoranthene	206-44-0	202	101
Pyrene	129-00-0	202	200
Benzo(a)anthracene	56-55-3	228	229
Chrysene	218-01-9	228	226
Benzo(b)fluoranthene	205-99-2	252	253
Benzo(k)fluoranthene	207-08-9	252	253
Benzo(a)pyrene	50-32-8	252	253
Indeno(1,2,3-cd)pyrene	193-39-5	276	138
Dibenz(a,h)anthracene	53-70-3	278	139
Benzo(g,h,i)perylene	191-24-2	276	138
Benzo(e)pyrene	192-97-2	252	253
2-Fluorobiphenyl-SS	321-60-8	172	171
Terphenyl-d(14)-SS	98904-43-9	244	122
Naphthalene-d(8)-IS	1520-96-3	136	68
Acenaphthene-d(10)-IS	15067-26-2	164	162
Phenanthrene-d(10)-IS	1517-22-2	188	94
Chrysene-d(12)-IS	1719-03-5	240	120
Perylene-d(12)-IS	1520-96-3	264	260

12.11. Quantitative Analysis- Quantitation is based on the integrated abundance of the target analytes' quantitation ion using the internal standard technique.

Table 12.4: Internal Standard Assignments

Compound	Internal Standard
Naphthalene	Naphthalene-d(8)-IS
2-Methylnaphthalene	Naphthalene-d(8)-IS
1-Methylnaphthalene	Naphthalene-d(8)-IS
Acenaphthylene	Acenaphthene-d(10)-IS
Acenaphthene	Acenaphthene-d(10)-IS
Fluorene	Acenaphthene-d(10)-IS
Phenanthrene	Phenanthrene-d(10)-IS
Anthracene	Phenanthrene-d(10)-IS
Fluoranthene	Phenanthrene-d(10)-IS
Pyrene	Chrysene-d(12)-IS
Benzo(a)anthracene	Chrysene-d(12)-IS
Chrysene	Chrysene-d(12)-IS
Benzo(e)pyrene	Perylene-d(12)-IS
Benzo(b)fluoranthene	Perylene-d(12)-IS
Benzo(k)fluoranthene	Perylene-d(12)-IS
Benzo(a)pyrene	Perylene-d(12)-IS
Indeno(1,2,3-cd)pyrene	Perylene-d(12)-IS
Dibenz(a,h)anthracene	Perylene-d(12)-IS
Benzo(g,h,i)perylene	Perylene-d(12)-IS
2-Fluorobiphenyl-SS	Acenaphthene-d(10)-IS
Terphenyl-d(14)-SS	Chrysene-d(12)-IS

13. Quality Control

13.1. **Table 13.1 – Batch Quality Control Criteria**

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per 20 samples. If analyzing a TCLP sample, the associated TCLP Blank must also be analyzed with the batch.	Target analytes must be less than reporting limit. If results are reported to MDL, target analytes in MB should be non-detect.	Re-analyze blank to confirm failure. Qualify results and/or re-extract associated samples. ***Exceptions:*** If sample ND, report sample without qualification; If sample result >10x MB detects, report sample If sample result <10x MB detects and sample cannot be re-extracted, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	Full Target List compounds	One per batch of up to 20 samples. LCSD is performed for water samples where no volume is provided for MS/MSD. In this instance, the batch data must be qualified with an M5 data qualifier.	Laboratory derived limits Full Target List: Marginal exceedances allowed according to the TNI standard.	Re-analyze the LCS to verify failure; If LCS passes, review samples for potential injection problems; If problem persists, check spike solution; Re-extract samples where possible. ***Exceptions:*** If LCS recovery is > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. Also, if the MS/MSD meet LCS QC limits the batch is acceptable.
Matrix Spike (MS)	Full Target List compounds	One per batch of up to 20 samples. If analyzing TCLP samples, one MS must be analyzed for each TCLP matrix.	Laboratory derived limits	If LCS and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences.
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One for every 5% of all environmental samples	Laboratory derived Limits	Report results with an appropriate footnote.

13.2. **Table 13.2 – Sample Quality Control Criteria**

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	Naphthalene-d8 Acenaphthene-d10 Phenanthrene-d10 Chrysene-d12 Perylene-d12	Added to all standards, samples, spikes, control samples, and method blanks prior to analysis	**Retention Time:** RT must be ± 30 seconds from last calibration check on all samples **Response:CCV I.S. areas must be** 50% to 200% of the area of the internal standardin the most recent calibration standard.	**Retention Time Failure:** If matrix interference is NOT probable, the analytical system must be checked for source of retention time shifting; Affected samples should be reanalyzed in the absence of an obvious instrument or matrix related interference.
Surrogate Standards	2-Fluorobiphenyl Terphenyl-d14	Added to all samples, spikes, control samples and method blanks prior to analysis	Laboratory derived limits	Re-analyze extract to confirm failure. Assess impact of sample matrix. In the absence of obvious matrix interference (high background, extremely dark extract), re-extract sample when possible or else report with appropriate footnote. ***Exceptions:*** Surrogate recovery above criteria and target compounds < RL, result may be reported with appropriate footnote. Surrogate recovery out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote.

14. Data Analysis and Calculations

14.1. **Raw Data Results:** The GC/MS data system will calculate the concentration of each analyte in the sample extract. If supplied with the preparation parameters, the system may be able to calculate the results back to the original matrix. The calculation for the concentration of the target analyte in the original matrix is listed below and is based on the calibration table in units of ppm (µg/mL). If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

14.1.1. Calculate response factors (RFs) for each compound as follows:

$$RF = (A_x C_{is})/(A_{is} C_x)$$

Where: A_x = Area of the characteristic ion for the compound being measured.
A_{ix} = Area of the characteristic ion for the specified internal standard.
C_{is} = Concentration of the specified internal standard (µg/mL).
C_x = Concentration of the compound being measure (µg/mL).

14.1.2. The percent relative standard deviation (%RSD) is calculated as follows:

$$\%RSD = \frac{s}{\bar{x}} \times 100\%$$

Where: s = Standard Deviation of initial response (see Section 14.1.1)
X = Mean of the Response Factors in Section 14.1.1

14.1.3. The Standard Deviation is calculated as follows:

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}}$$

Where: x_i = Each individual response factor
N = Number of the Response factors mentioned above.

14.1.4. The Relative Percent Difference (%D) is calculated as follows:

$$\%Difference = \frac{|RF_i - RF_c|}{RF_i} \times 100$$

Where: RF_i = Average response factor from initial calibration
RF_c = Response factor from current verification check standard.

14.1.5. Results Calculation- Aqueous Samples:

$$\text{Concentration } (\mu\text{g/L}) = \frac{(C_x)(V_x)(DF)}{(V_s)}$$

Where: C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
V_s = Volume of water sample extracted (mL).

14.1.6. Results Calculation- Soil/Solid Samples:

$$\text{Concentration } (\mu\text{g/kg}) = \frac{(C_x)(V_x)(1000)(DF)}{(W_s)}$$

Where: C_x = Concentration in extract (µg/mL).
V_v = Volume of final extract (mL).
DF = Dilution factor.
W_s = Weight of soil sample extracted (g).

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. Refer to Tables 12.2, 13.1 and 13.2.

16. Corrective Actions for Out-of-Control Data

16.1. Refer to Tables 12.2, 13.1 and 13.2.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. Refer to Tables 12.2, 13.1 and 13.2.

18. Method Performance

18.1. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually per S-GB-Q-020, *Determination of the LOD and LOQ* (most current revision or replacement) for each matrix per instrument.

18.2. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, *Orientation and Training Procedures* (most current revision or replacement).

19. Method Modifications

19.1. Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.

19.2. All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.

19.3. Procedures identified as “Best Practices” by the PACE 3P Program will be incorporated into the document as minimum requirements for Pace laboratories.

19.4. ()(The Low Volume Extraction is a modification which the sample volume used for extraction purposes is reduced to 100 mL with the solvent volume reduced to 6 mL to keep the sample to solvent ratio correct.

19.5. The lab practice is to have thermal preservation at ≤6˚C. This is based on 40CFR Part 136, page 29808, footnote 18.

19.6. The laboratory follows the DFTPP Tune criteria outlined in EPA 525.2.

19.7. If a client fails to provide the method required Matrix Spike/Matrix Spike Duplicate (MS/MSD), the laboratory will analyze a Laboratory Control Spike Duplicate to demonstrate precision. The analytical batch will be qualified with the “M5” data qualifier.

20. Instrument/Equipment Maintenance

20.1. Please refer to the instrument operations manual or the SOP S-GB-Q-008, *Preventative, Routine, and Non-routine Maintenance* (current revision or replacement).

21. Troubleshooting

21.1. Please refer to the instrument manufacturer operations manual.

22. Safety

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets

(SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

22.3. **Equipment:** Portions of the analytical instrumentation operate at high temperatures and under positive pressure. Care must be taken to minimize accidents and injuries when working on or with this equipment. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones. The GC pneumatic system uses gas under high pressure. This high pressure introduces the risk of injury due to flying glass and other objects should a vessel or line rupture. Safety glasses are highly recommended at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-GB-W-001, *Waste Handling and Management* (most current revision or replacement).

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires).

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. USEPA, SW-846, Method 8270C, "Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), December 1996.

25.2. USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

25.3. USEPA, Method 625, Appendix A to Part 136, (1984), "Base/Neutrals and Acids".

25.4. USEPA, Method 525.2, Revision 2.0 (1995), "Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry".

25.5. Pace Quality Assurance Manual- most current version.

25.6. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.7. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Not applicable to this SOP.

27. Revisions

Document Number	Reason for Change	Date
S-GB-O-050-Rev.03	Throughout Document: Updated SOP format to be consistent with SOP: S-GB-Q-017 *Preparation of SOPs*. Throughout Document: Updated table references to coincide with their proper number format. Table 11.2: Updated DFTPP Tune Criteria to be consistent with EPA 525.2. Section 11.3.2 and Table 11.4: Updated ICV criteria to match CCV criteria and calculations. Section 25: Added EPA 525.2 reference.	27Jan2014
S-GB-O-050-Rev.04	Table 7.1: Removed 1L glass Amber. Table 9.1/12.1: Deleted 40MSS3, changed 40MSS8 to 40MSSS9. Table 9.2: Removed MACH unit information. Table 10.1 and Section 10.6: Added Acetone and changed from DCM to acetone. Table 10.8.1: Removed Aqueous. Section(s) 10.8.2.1.2, 10.8.3.2, 10.8.4.2, 10.8.5.2, 10.8.6.2, 10.8.7.2., Table 11.2. and throughout document: Removed HVI aqueous information, merged into normal aqueous analytical procedure. Table 11.1 and 11.3: Updated with current CAL information. Section 11.3.1: Added CRDL information. Table 11.4.2: Updated to current practice. Table 13.1 Updated MB criteria from 20X to 10X detection rules. Section(s) 12.3 and 12.4 Breakdown and tailing criteria, Deleted. Throughout SOP: Updated numbering and converted Inc to LLC.	24Oct2016

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STANDARD OPERATING PROCEDURE

Determination of Volatile Organics by GC/MS

Reference Methods: EPA Method SW-846 8260B with 5030B and 5035; and EPA Method 624

LOCAL SOP NUMBER:	S-GB-O-056-Rev.11
EFFECTIVE DATE:	Date of Final Signature
SUPERSEDES:	S-GB-O-056-Rev.10
SOP TEMPLATE NUMBER:	TMP-ALL-O-002-Rev.01

LOCAL APPROVAL

Nils Melberg, Laboratory General Manager — Date: 06/21/17

Kate Verbeten, Laboratory Quality Manager — Date: 6/21/17

Scott Turner, Department Manager — Date: 6/21/2017

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL.

Signature	Title	Date

This is **COPY#** ____ Distributed on _____ by _____ and is ____ **CONTROLLED**

Table of Contents

1. Purpose/Identification of Method

This Standard Operating Procedure (SOP) documents the procedures used by PASI – Green Bay to determine the concentration of Volatile Organic Compounds (VOCs) in environmental samples. The laboratory utilizes purge-and-trap GC/MS and bases these documented procedures on those listed SW-846 Methods 5030B, 5035 and 8260B; and EPA 624.

2. Summary of Method

Volatile organic compounds are introduced into the gas chromatograph by a purge-and trap method. The analytes are purged from a sample aliquot or extract by purging with helium or nitrogen. The purged analytes are collected in a trap. At the completion of the purge time, the trap is rapidly heated and back flushed with helium to drive out the trapped analytes. The analytes are transferred into the inlet of a capillary gas chromatography column. The carrier gas flow through the column is controlled and the temperature is increased according to a set program to achieve optimum separation of purged analytes. The mass spectrometer is operated in a repetitive scan mode. Analytes are identified by the GC/MS retention times and by a comparison of their mass spectra with spectra of authentic standards. Analytes are quantified by comparing the response of a selected primary ion relative to an internal standard against a calibration curve.

3. Scope and Application

3.1. **Personnel:** This procedure is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap GC/MS systems and interpretation of GC/MS data. Each analyst must demonstrate the capability to generate acceptable results with this method to be considered qualified to report sample results.

3.2. **Parameters:** This SOP applies to compounds listed in Section 11, Table 11.1 Calibration standard compound concentrations, analyzed by SW-846 Methods 5030B, 5035 and 8260B and EPA 624.This method is applicable to most organic compounds that have boiling points below 200ºC and are insoluble or slightly soluble in water. Volatile water-soluble compounds may also be determined although quantitation limits are typically higher due to their hydrophilic properties (e.g. ketones, oxygenates). This method cannot be substituted for other similar published methods where permit or regulatory compliance is required.

4. Applicable Matrices

4.1. This SOP is applicable to most water and solid samples, regardless of moisture content. Common matrices are ground and surface water, wastewater, aqueous sludge, sediment, soils, and other solid samples. Procedures may need to be adapted to address limits in the method or equipment that might hinder or interference with sample analysis. All adaptations made to address matrix related modifications must be documented within the analytical data.

5. Limits of Detection and Quantitation

5.1. The reporting limit (PQL) for all analytes can be found Section 11, Table 11.1. All current MDLs are listed in the LIMs and are available by request from the Quality Manager.

6. Interferences

6.1. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the absorbent trap. The use of polytetrafluoroethylene (PTFE, Teflon) as thread sealants, tubing, or in flow controllers is highly recommended since other materials can be sources of contamination which may concentrate in the trap during the purging.

6.2. A common source of interfering contamination is carryover. This may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive action to this condition is rinsing the purging apparatus and sample syringes with two or more portions of organic free water between samples. Analyze one or more blanks to check for cross contamination prior to sample analysis.

6.3. Since methylene chloride and acetone are common laboratory solvents, special precautions must be taken. The volatiles analysis and sample storage area should be located as far as possible from areas where these solvents are used or stored. Where possible, the volatiles analysis and sample storage area should be served by a separate HVAC system and maintained under positive pressure to prevent intrusion of contaminants. Laboratory clothing previously exposed to methylene chloride fumes during extraction procedures can contribute to sample contamination.

7. Sample Collection, Preservation, Shipment and Storage

Table 7.1: Sample Collection, Preservation, Storage and Hold time.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Three (3) VOA vials	Acidified w/ 1:1 HCl (1-2 drops) to pH<2, no headspace *Note:* 2-CLEVE, Styrene, and Vinyl Chloride requires an unpreserved sample.	≤6°C	Unpreserved: 7 days pH Preserved: 14 days
Low Level Aliquot Soil/Solid (non-aqueous)	One (1) 2-4 oz. wide mouth jar for % moisture **AND** Two (2) 5-g aliquots in vials with magnetic stir bar, 5.0 mL reagent water and 1.0 g sodium bisulfate as needed. *OR (alternative):* Two (2) EnCore, TerraCore or similar sampling tubes.	No preservation *OR* sodium bisulfate **Note:** If sample effervesces on contact with the preservative, the sodium bisulfate should be eliminated for that sample.	With sodium bisulfate: ≤6°C Without preservation (including EnCore, TerraCore or similar): 4 ± 2°C for up to 48 hours before storing between -7°C and -20°C, inclusive, until analysis.	Unpreserved or not stored frozen: 48 hours Preserved with sodium bisulfate or stored frozen: 14 days
High Level Aliquot Soil/Solid (non-aqueous)	One (1) 10-g aliquot in vial with 10.0 mL purge and trap grade MeOH. *OR (alternative)* One (1) 10-g aliquot in empty vial	Methanol - if sample was collected in empty vial it must be transferred into 10 mL of purge & trap grade MeOH within 48 hours of collection	With methanol: ≤6°C.	Unpreserved: 48 hours Preserved with methanol: 14 days WI Only: 21 days
TCLP Leachates	Tedlar bag or THREE (3) VOA vials.	Filled and capped to eliminate any headspace. Vials with bubbles larger than 5 mm should be discarded.	≤6°C	14 days from end of leaching procedure

Table 7.2: Trip Blank Requirements

Aqueous	Low Level Aliquot Soil/Solid	High Level Aliquot Soil/Solid
One (1) 40mL VOA vial w/ reagent DI water	One (1) 40mL VOA vial w/ 5mL sodium bisulfate (or reagent DI water) and magnetic stir bar	One (1) 40mL VOA vial w/ 5mL purge and trap grade MeOH

8. Definitions

Refer to Glossary section of the Pace Quality Assurance Manual (QAM) for a comprehensive list of terms and definitions. In addition to those listed in the QAM, the following are additional terms found in this SOP.

8.1. **Run Sequence Log** – A logbook that lists all injections and analyses performed on a particular piece of equipment regardless of the use of the data collected from each analysis.

8.2. **Toxicity Characteristic Leaching Procedure (TCLP)** – An extraction procedure used to determine if a sample is acceptable for upland disposal. The extraction procedure is meant to simulate the leaching of contaminants under the environmental conditions typically found in a landfill.

8.3. **Tune Period** – The period after the BFB instrument tune check within which analyses may be performed.

9. Equipment and Supplies

Table 9.1: Equipment

Analytical Instrument/Peripherals	EPIC Pro Name
HP 5890 Series II GC	40MSV1
HP 5972 MSD	40MSV1
Archon Autosampler	40MSV1
Tekmar 3000 Purge and Trap Concentrator	40MSV1
HP 6890 GC	40MSV2
HP 5973 MSD	40MSV2
Archon Autosampler	40MSV2
Tekmar 3000 Purge and Trap Concentrator	40MSV2
Agilent 6850 GC	40MSV3
Agilent 5975 MSD	40MSV3
Tekmar Aquatek 70	40MSV3
Tekmar Stratum Purge and Trap Concentrator	40MSV3
HP 6890 GC	40MSV5
HP 5973 MSD	40MSV5
Archon Autosampler	40MSV5
Tekmar 3000 Purge and Trap Concentrator	40MSV5
HP 6890 GC	40MSV7
HP 5973 MSD	40MSV7
Archon Autosampler	40MSV7
Tekmar 3000 Purge and Trap Concentrator	40MSV7
Agilent Technologies 6850 Network GC System	40MSV8
Agilent Technologies 5975B MSD	40MSV8
EST 8100 Autosampler	40MSV8
Teledyne Tekmar 14-9800-100 Stratum Purge and Trap System	40MSV8
Agilent 5975C GCMS	40MSVA
Agilent 7890A GC	40MSVA
EST 8100 Autosampler	40MSVA
Tekmar Stratum Purge and Trap Concentrator	40MSVA
Agilent 5975C GCMS	40MSVB
Agilent 7890A GC	40MSVB
Tekmar Atomx Autosampler/Purge and Trap Conc.	40MSVB
Agilent 7890B GC	40MSVC
Agilent 5977A MSV	40MSVC
Tekmar Stratum Purge and Trap Concentrator	40MSVC
EST Centurion Autosampler	40MSVC

Table 9.2: Supplies

Supplies	Manufacturer	Vendor	Catalog #
10µL Gastight 1701	Hamilton	Fisher Scientific	14-815-1
25µL Gastight 1702	Hamilton	Fisher Scientific	14-815-29
50µL Gastight 1705	Hamilton	Fisher Scientific	14-824-30
100µL Gastight 1710	Hamilton	Fisher Scientific	13-684-100
250µL Gastight 1725	Hamilton	Fisher Scientific	13-684-102
500µL Gastight 1750	Hamilton	Fisher Scientific	13-684-106
1mL Gastight 1001	Hamilton	Fisher Scientific	14-824-25
5mL Gastight 1005	Hamilton	Fisher Scientific	13-684-96
50mL Gastight 1050	Hamilton	Fisher Scientific	14-815-195
DB-624 Capillary column, 20mX0.18 mm i.d.X1.0 µm	J&W Scientific	VWR Scientific	121-1324
K-Trap, Vocarb3000, Tekmar3000	Supelco	Supelco	24920-U
Fritless 5 mL Sparge Tube	Supelco	Supelco	22780
IceBlue Septa, 11mm	Restek	Restek	22392
Single Gooseneck Injection port liners (4mm)	Restek	Restek	20799
Gold-plated inlet seals	Restek	Restek	21306
Viton O-rings	Restek	Restek	20377
0.4mm Vespel/Graphite ferrules	Restek	Restek	20211
GCMS Filaments	Agilent Technologies	Agilent Technologies	05972-60053
Stir Bar	Fisher Brand	Fisher Brand	14-511-60A
40 mL VOA vials	QEC	QEC	3112-40mL
10 mL volumetric	Kimax Brand	Fisher Scientific	10-212AA
25 mL volumetric	Kimax Brand	Fisher Scientific	10-212BB
50 mL volumetric	Kimax Brand	Fisher Scientific	10-212A
100 mL volumetric	Kimax Brand	Fisher Scientific	10-212B
200 mL volumetric	Kimax Brand	Fisher Scientific	10-212C
500 mL volumetric	Kimax Brand	Fisher Scientific	10-218D
Pasteur Pipettes	Fisher Scientific	Fisher Scientific	13-678-20A
Pipette bulb	Fisher Scientific	Fisher Scientific	14-065B
0.1-2.5 mL Repipettor	Brinkmann	Fisher Scientific	13-688-130
1-5 mL Repipettor	Brinkmann	Fisher Scientific	13-688-131
2-10 mL Repipettor	Brinkmann	Fisher Scientific	13-688-133
5-25 mL Repipettor	Brinkmann	Fisher Scientific	13-688-134
1.8 mL amber vials & caps	Restek	Restek	24637
10 mL graduate cylinder	Kimax Brand	Fisher Scientific	08-554B “to deliver”
40 mL VOA vials HCl preserved	QEC	QEC	3112-40HCl
2 oz. jars with Teflon lids	QEC	QEC	2114-0002
Spatulas	Fisher Scientific	Fisher Scientific	14-511-60A

10. Reagents and Standards

10.1. Reagents

Table 10.1: Reagents

Reagent	Conc.	Purity	Manufacturer	Vendor	Catalog #
Methanol	100%	Purge and Trap grade	Burdick & Jackson	VWR Scientific	232-1
Sodium Bisulfate	Granular	Certified grade	Fisher Scientific	Fisher Scientific	S-240-3
Nitrogen gas		99.999%	Michigan Airgas	Michigan Airgas	
Helium gas		99.999%	Michigan Airgas	Michigan Airgas	
Reverse Osmosis (ROW) Water		Organic Free	Flowmatic	Culligan	
Ottawa Sand, 20-30 mesh		ASTM C190	Fisher Scientific	Fisher Scientific	S23-3

10.2. Analytical Standards

10.2.1. Definitions: Standards are required for mass spectrometer tuning, initial calibration, calibration verification standards, second source verification, internal standards, surrogates, and for preparing LCS, MS, and MSD samples. Table 10.2 describes the standards used. Table 10.3 lists the stock standards used. Table 10.4 lists the compounds in each stock standard.

Table 10.2: Standard Definitions

Standard	Description	Comments
Tune Standard	4-Bromofluorobenzene (BFB) solution used to verify ion response ratios prior to analysis	Must purge between 5 and 50ng
Initial Calibration Standards	Standards prepared at varying levels to determine response and retention characteristics of instrument	Method requires a minimum of 5 levels
Continuing Calibration Verification Standard	A calibration standard prepared at mid-level concentration for all target compounds. This standard is used to verify that the instrument response has not changed significantly since the initial calibration was performed.	
Second Source Verification Standard	A standard prepared from a source other than that used for the initial calibration. This mid-level standard verifies the accuracy of the calibration curve.	For volatiles analysis, this may be used as the LCS if analyzed once every 20 samples.
Internal Standard	A solution added all standards, samples, spikes, control samples, and method blanks prior to analysis. This standard is used to adjust response ratios to account for instrument drift.	Pentafluorobenzene 1,4-Difluorobenzene Chlorobenzene-d5 1,4-Dichlorobenzene-d4
Surrogate Standard	A solution added to all samples, spikes, control samples, and method blanks prior to analysis.	Dibromofluoromethane Toluene-d8 4-Bromofluorobenzene
Spiking Standard	This solution contains all target analytes and should not be prepared from the same standards as the calibration standards.	For volatiles analysis, this can be used as the second source verification standard.

10.2.2. Stock Standards

Table 10.3: Stock Standards

Standard	Conc.	Purity	Manufacturer	Vendor	Catalog #
4-BFB Tuning Standard	5000 µg/mL	99%	Restek	Restek	30003-520
502.2 Cal Gases Mix	2000 µg/mL	99%	Restek	Restek	30042
502.2 ICV Gases Mix	2000 µg/mL	99%	Accustandard	Accustandard	M-502B-10X
502.2 Cal 2000 Megamix	2000 µg/mL	99%	Restek	Restek	30431
Megamix – ICV	2000 µg/mL	99%	o2si	o2si	122708-05
Vinyl Acetate	Neat	99+%	Chem Service	Chem Service	F718
Calibration Ketone Mix	5000 µg/mL	99%	Restek	Restek	30006
Ketones – ICV	2000 µg/mL	99%	o2si	o2si	121020-10
Pace GB Custom Mix #3	various µg/mL	99+%	o2si	o2si	120407-11-SS
Custom – ICV	100,000 – 200,000 µg/µL	99%	o2si	o2si	122707-05
Acrolein – CAL	Neat	99+%	Chem Service	Chem Service	N-11030-1G
2-Chloroethylvinyl Ether	2000 µg/mL	99+%	Restek	Restek	30265
Reactive Mix – ICV	100-1000 µg/mL	99%	o2si	o2si	120407-13
8260 Internal Standard	2500 µg/mL	99%	Restek	Restek	30173
8260 Surrogate Standard	2500 µg/mL	99%	Restek	Restek	30174
CLP 4.1Mega Mix	2000 µg/mL	99%	Restek	Restek	30456
502.2 Gases Mix #1	2000 µg/mL	99%	Restek	Restek	30006

10.2.3. Standard Mixes

Table 10.4: Standard Mixes

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
Restek	**4-BFB Tuning Standard**	**30003-520**	4-bromofluorobenzene	2500
Restek	**502.2 Cal Gases Mix**	**30042**	Bromomethane	2000
			Chloroethane	2000
			Chloromethane	2000
			Dichlorodifluoromethane	2000
			Trichlorofluoromethane	2000
			Vinyl Chloride	2000
Accustandard	**502.2 ICV Gases Mix =**	**M-502B-10X**	Bromomethane	2000
			Chloroethane	2000
			Chloromethane	2000
			Dichlorodifluoromethane	2000
			Trichlorofluoromethane	2000
			Vinyl Chloride	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
Restek	**502.2 Cal 2000 MegaMix**	**30431**	1,1,1,2-Tetrachloroethane	2000
			1,1,1-Trichloroethane	2000
			1,1,2,2-Tetrachloroethane	2000
			1,1,2-Trichloroethane	2000
			1,1-Dichloroethane	2000
			1,1-Dichloropropene	2000
			1,1-Dichlroethene	2000
			1,2,3-Trichlorobenzne	2000
			1,2,3-Trichloropropane	2000
			1,2,3-Trimethylbenzene	2000
			1,2,4-Trimethylbenzene	2000
			1,2-Dibromo-3-chloropropane	2000
			1,2-Dibromoethane	2000
			1,2-Dichlorethane	2000
			1,2-Dichlorobenzene	2000
			1,2-Dichloropropane	2000
			1,3,5-Trimethylbenzene	2000
			1,3-Dichlorobenzene	2000
			1,3-Dichloropropane	2000
			1,4-Dichlorobenzene	2000
			2,2-Dichloropropane	2000
			2-Chlorotoluene	2000
			4-Chlorotoluene	2000
			4-Isopropyltoluene	2000
			Benzene	2000
			Bromobenzene	2000
			Bromochloromethane	2000
			Bromodichloromethane	2000
			Bromoform	2000
			Carbon Tetrachloride	2000
			Chlorobenzene	2000
			Chloroform	2000
			cis-1,2-Dichloroethene	2000
			cis-1,3-Dichloropropene	2000
			Dibromochloromethane	2000
			Dibromomethane	2000
			Ethylbenzene	2000
			Hexachloro-1,3-butadiene	2000
			Isopropylbenzene	2000
			Methylene Chloride	2000
			m-Xylene	2000
			Naphthalene	2000
			n-Butylbenzene	2000
			n-Propylbenzene	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
			o-Xylene	2000
			p-Xylene	2000
			sec-Butylbenzene	2000
			Styrene	2000
			tert-Butylbenzene	2000
			Tetrachloroethene	2000
			Toluene	2000
			trans-1,2-Dichloroethene	2000
			trans-1,3-Dichloropropene	2000
			Trichloroethene	2000
o2si	**MegaMix – ICV**	**122708-05**	Isopropyl alcohol	20,000
			Isobutyl alcohol	20,000
			tert-butyl alcohol	10,000
			Acetonitrile	5000
			Ethyl ether	2000
			Isopropyl ether	2000
			Benzene	2000
			n-propylbenzene	2000
			sec-butylbenzene	2000
			tert-butylbenzene	2000
			1,2,4 trimethylbenzene	2000
			n-butylbenzene	2000
			naphthalene	2000
			p-cymene	2000
			1,2-dichlorobenzene	2000
			1,3-dichlorobenzene	2000
			Chlorobenzene	2000
			1,2,3-trichlorobenzene	2000
			1,2,4-trichlorobenzene	2000
			Bromobenzene	2000
			Bromochloromethane	2000
			Carbon tetrachloride	2000
			Dibromomethane	2000
			Bromodichloromethane	2000
			Bromoform	2000
			Dibromochloromethane	2000
			trans-1,2-dichloroethylene	2000
			1,1-dichloroethylene	2000
			1,1-dichloroethane	2000
			1,1,1-trichloroethane	2000
			2,2-dichloropropane	2000
			tetrachloroethylene	2000
			1,1,1,2-tetrachloroethane	2000
			1,1,2-trichloroethane	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
			1,2-dichloroethane	2000
			1,2-dibromo-3chloropropane	2000
			1,2-dibromomethane	2000
			1,1 dichloropropylene	2000
			1,2,3-trichloropropane	2000
			1,2 dichloropropane	2000
			trans-1,3-dichloropropylene	2000
			cis-1,3-dichloropropylene	2000
			1,3-dichloropropane	2000
			Iodomethane	2000
			Carbon disulfide	2000
			Methyl acetate	2000
			Cyclohexane	2000
			Methyl t-butyl ether	2000
			Ethyl t-butyl ether	2000
			tert-amyl methyl ether	2000
			1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113)	2000
			Heptane (C7)	2000
			1,2,3-trimethylbenzene	2000
			n-hexane (C6)	2000
			Isopropyl acetate	2000
			1-methylnaphthalene	2000
			2-methylnaphthalene	2000
			Acrylonitrile	2000
			Allyl chloride	2000
			Chloroform	2000
			2-chlorotoluene	2000
			4-chlorotoluene	2000
			Cis-1,2-dichloroethylene	2000
			1,4-dichlorobenzene	2000
			Cis-1,4-dichloro-2-butene	2000
			2,3-dichloro-1-propene	2000
			Ethylbenzene	2000
			Hexachlorobutadiene	2000
			Hexachloroethane	2000
			Isopropylbenzene	2000
			Methyl cyclohexane	2000
			Methylene chloride	2000
			Styrene	2000
			1,1,2,2-tetrachloroethane	2000
			Tetrahydrofuran	2000
			Toluene	2000
			Trichloroethylene	2000
			1,3,5-Trimethylbenzene	2000
			m-xylene	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
			o-xylene	2000
			p-xylene	2000
Chem Service	**Vinyl Acetate**	**F718**	Vinyl Acetate	Neat
Restek	**Calibration Ketone Mix**	**30006**	2-Butanone	5000
			2-Hexanone	5000
			4-Methyl-2-pentanone	5000
			Acetone	5000
o2si	**Ketones – ICV**	**121020-10**	2-Butanone	2000
			2-Hexanone	2000
			4-Methyl-2-pentanone	2000
			Acetone	2000
o2si	**Pace-GB Custom**	**121082-01-SS**	Dichlorofluoromethane	2000
	Mix #3		1,1,2-trichlorotrifluoroethane	2000
			Acetonitrile	5000
			Iodomethane (methyl iodide)	2000
			Allyl chloride (3-chloropropene)	2000
			Carbon disulfide	2000
			Acrylonitrile	2000
			2,3-dichloropropylene	2000
			cis-1,4-dichloro-2-butene	2000
			trans-1,4-dichloro-2-butene	2000
			1,2,3-trimethylbenzene	2000
			Hexachloroethane	2000
			2-methylnaphthalene	2000
			1-methylnaphthalene	2000
			Ethanol	100,000
			Diethyl ether (ethyl ether	2000
			2-propanol (isopropanol)	20,000
			tert-butanol (TBA)	10,000
			Methyl acetate	2000
			n-Hexane	2000
			Methyl-tert-butyl-ether (MTBE)	2000
			1-Propanol	100,000
			1,4-dioxane	100,000
			1-butanol	100,000
			Tetrahydrofuran	2000
			Cyclohexane	2000
			Heptane (C7)	2000
			tert-amyl methyl ether	2000
			Ethyl t-butyl ether	2000
			Isopropyl ether	2000
			Isobutyl alcohol	20,000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
			Methyl cyclohexane	2000
			Isopropyl acetate	2000
Chem Service	**Acrolein - Cal**	**N-11030-1G**	Acrolein	Neat
Restek	**2-chloroethylvinyl ether**	**30265**	2-chloroethylvinyl ether	2000
o2si	**Reactive Mix – ICV**	**120407-13**	2-chloroethylvinyl ether	100
			Acrolein	1000
			Vinyl Acetate	100
Restek	**8260 Internal Standard**	**30173**	Pentafluorobenzene	2500
			1,4-Difluorobenzene	2500
			Chlorobenzene-d5	2500
			1,4-Dichlorobenzene-d4	2500
Restek	**8260 Surrogate Standard**	**30174**	Dibromofluoromethane	2500
			Toluene-d8	2500
			1-Bromo-4-fluorobenzene	2500
Restek	**CLP 4.1Mega Mix**	**30456**	1,1,2-trichlorotrifluoroethane	2000
			1,1-dichloroethene	2000
			Benzene	2000
			Bromodichloromethane	2000
			Bromoform	2000
			Carbon Tetrachloride	2000
			Chlorobenzene	2000
			Chloroform	2000
			Dibromochloromethane	2000
			1,2-dichloroethane	2000
			Cis-1,2-dichloroethene	2000
			1,2-Dichloropropane	2000
			trans-1,3-dichloropropylene	2000
			cis-1,3-dichloropropylene	2000
			Ethylbenzene	2000
			Styrene	2000
			1,1,2,2-tetrachloroethane	2000
			Tetrachloroethene	2000
			Toluene	2000
			1,1,1-trichloroethane	2000
			1,1,2-trichloroethane	2000
			Trichloroethane	2000
			m&p-Xylene	4000
			o-Xylene	2000

Vendor	Standard Name	Catalog#	Compound list	Concentration (µg/mL)
			Cyclohexane	2000
			Methylcyclohexane	2000
			1,2-dibromo-3chloropropane	2000
			1,2-Dibromoethane	2000
			Isopropylbenzene	2000
			1,2,4-Trichlorobenzene	2000
			1,3-Dichlorobenzene	2000
			1,4-Dichlorobenzene	2000
			1,2-Dichlorobenzene	2000
			Methyl acetate	2000
			Carbon disulfide	2000
			Methylene chloride (dichloromethane)	2000
			Methyl-tert-butyl ether (MTBE)	2000
			Trans-1,2-dichloroethene	2000
			1,1-dichloroethane	2000

10.2.4. Standard Storage Conditions

Table 10.5: Analytical Standard Storage Conditions

Standard Type	Description	Expiration	Storage
Stock Solutions	Concentrated reference solution purchased directly from approved vendor	1. Manufacturer's recommended expiration date for unopened ampulated standards. 2. Gas standards must be replaced 6 months after ampule is opened. 3. All other stock standards must be replaced 6 months after ampule is opened or on expiration date, whichever is sooner.	1. Manufacturer's recommended storage conditions 2. When standard is opened, record all information in the standard logbook.
Intermediate and Working Standard Solutions	Reference solutions prepared by dilutions of the stock solution	1. 6 months from preparation or the expiration date listed for the stock source, whichever is sooner. 2. 6 months for gas working standards. 3. Working solutions must be checked frequently and replaced if degradation or evaporation is suspected.	1. Store in amber vials with Teflon lined screw caps 2. Manufacturer's recommended storage conditions for stock source solution. 3. If stock source conditions conflict, store standard at coldest condition of any source.

10.2.5. Standard Sources

Standards are prepared from commercially available multi-compound stock solutions and neat materials by multiple dilutions. The sources of the stock solutions and neat materials are listed in Table 10.3. The recipes for preparing dilutions and all working and intermediate standards, and concentrations for all compounds are presented in Tables 10.6 and 10.7. All intermediate standards are prepared using purge and trap grade methanol and stored frozen in glass vials with Teflon lined screw caps or Mininert valves or as recommended by the standard manufacturer.

10.2.6. Preparation Procedures

Table 10.6: Intermediate Standard Preparation

Standard	Acronym	Concentration	Direction found in Section:
Level 1 Calibration Standard (MeOH Curve Only)	CAL1 (MeOH Curve Only)	0.40µg/L all compounds except as follows: 1.0 µg/L acetonitrile; 2.0 µg/L tert butyl alcohol; 4.0 µg/L acrolein, isopropanol, isobutanol; 20 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Table 10.7
Water Level 1 Calibration Standard MeOH Level 2 Calibration Standard	CAL1 (Water) CAL2 (MeOH)	1.0µg/L all compounds except as follows: 2.5 µg/L acetonitrile; 5.0 µg/L tert butyl alcohol; 10 µg/L acrolein, isopropanol, isobutanol; 50 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Table 10.7
Water Level 2 Calibration Standard MeOH Level 3 Calibration Standard	CAL2 (Water) CAL3 (MeOH)	5.0 µg/L all compounds except as follows: 12.5 µg/L acetonitrile; 25 µg/L tert butyl alcohol; 50 µg/L acrolein, isopropanol, isobutanol; 250 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Water Level 3 Calibration Standard MeOH Level 4 Calibration Standard	CAL3 (Water) CAL4 (MeOH)	20 µg/L all compounds except as follows: 50 µg/L acetonitrile,; 100 µg/L tert butyl alcohol; 200 µg/L acrolein, isopropanol, isobutanol; 1000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Water Level 4 Calibration Standard MeOH Level 5 Calibration Standard	CAL4 (Water) CAL5 (MeOH)	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Table 10.7
Water Level 5 Calibration Standard MeOH Level 6 Calibration Standard	CAL5 (Water) CAL6 (MeOH)	100 µg/L all compounds except as follows: 250 µg/L acetonitrile; 500 µg/L tert butyl alcohol; 1000 µg/L acrolein, isopropanol, isobutanol; 5000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Water Level 6 Calibration Standard MeOH Level 7 Calibration Standard	CAL6 (Water) CAL7 (MeOH)	200 µg/L all compounds except as follows: 500 µg/L acetonitrile; 1000 µg/L tert butyl alcohol; 2000 µg/L acrolein, isopropanol, isobutanol; 10000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Level 7 Calibration Standard (Water Curve only)	CAL7 (Water Curve only)	300 µg/L all compounds except as follows: 750 µg/L acetonitrile; 1500 µg/L tert butyl alcohol; 3000 µg/L acrolein, isopropanol, isobutanol; 15000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
*Optional Water Level 3 Calibration	CAL3 (Water	10 µg/L all compounds except as follows:	Table 10.7

Standard	Acronym	Concentration	Direction found in Section:
Standard * If this standard is made for a water Curve, all subsequent Water Level # will increment by 1 (i.e. 300µg/L will now be CAL8)	Curve only) *Optional	25 µg/L acetonitrile; 50 µg/L tert butyl alcohol; 100 µg/L acrolein, isopropanol, isobutanol; 500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	
Independent Calibration Verification Standard	ICV050	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Calibration Verification Standard	CCV050	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Table 10.7
Acrolein – Cal Intermediate	Acrolein - Cal	20,000 µg/mL	Table 10.7
Vinyl Acetate – Cal Intermediate	Vinyl Acetate - Cal	10,500 µg/mL	Table 10.7
Surrogate Standard	SS	50 µg/L	Table 10.7
Internal Standard	IS	50 µg/L	Table 10.7
Method Blank	MB	< Reporting Limit	Table 10.7
BFB	TUNExxx	50 ng injection	Table 10.7
Matrix Spike/ Lab Control Spike Stock Solution - CLP 4.1List for Water and Low Level Soil Samples	MS/LCS CLP 4.1 List Stock Solution for Water and Low Level Soil Samples	100 µg/mL for all compounds	Table 10.7
Matrix Spike/Lab Control Spike Stock Solution - CLP 4.1 List for Methanol Preserved Soil Samples	MS/LCS CLP 4.1 List Stock Solution for Methanol Preserved Soil Samples	500 µg/mL for all compounds	Table 10.7
Matrix Spike/Lab Control Spike Stock Solution - Full List for Water and Low Level Soil Samples	MS/LCS Stock Solution – Full List for Water and Low Level Soil Samples	100 µg/mL all compounds except as follows: 1000 µg/mL Acrolein	Table 10.7
Matrix Spike/ Lab Control Spike Stock Solution - Full List for Methanol Preserved Soil Samples	MS/LCS Stock Solution – Full List for Methanol Preserved Soil Samples	500 µg/mL all compounds except as follows: 5000 µg/mL Acrolein	Table 10.7
MS/MSD – LCS/LCSD Spike for Water	MS/MSD	50 µg/L for most compounds, Various for	Table 10.7

Standard	Acronym	Concentration	Direction found in Section:
Samples	LCS/LCSD	others.	
MS/MSD – LCS/LCSD Spike for 624 Water Samples	MS/MSD LCS/LCSD	20 µg/L for most compounds, Various for others.	Table 10.7
MS/MSD – LCS/LCSD Spike for Low Level Soil Samples	MS/MSD LCS/LCSD	50 µg/kg for most compounds, Various for others.	Table 10.7
MS/MSD – LCS/LCSD Spike for Methanol Preserved Soil Samples	MS/MSD LCS/LCSD	2500 µg/kg for most compounds, Various for others.	Table 10.7
Extraction Blank	EBLK	< Reporting Limit	

Table 10.7: Preparation of Standards

Standard	Acronym	Concentration of Intermediate	Reagents Used	Final Volume
4-Bromofluorobenzene	BFB	50 µg/mL	100µL of 5000 µg/mL BFB into methanol	10 mL
Internal Standard	IS	250 µg/mL	5000 µL of 2500 µg/mL IS into methanol	50 mL
Surrogate Standard	SS	250 µg/mL	5000 µL of 2500 µg/mL SS into methanol	50 mL
Internal/Surrogate Std.	IS/SS	250 µg/mL	5000 µL of 2500 µg/mL IS/SS into MeOH	50 mL
Vinyl Acetate – Cal Intermediate	Vinyl Acetate - Cal	10,500 µg/mL	0.105g of neat Vinyl Acetate Diluted into methanol	10 mL
Acrolein – Cal Intermediate	Acrolein - Cal	20,000 µg/mL	0.21g of neat Acrolein 1 mL Reverse Osmosis Water Diluted into methanol	10 mL
100 µg/mL Calibration Std. 250 µg/mL acetonitrile; 500 µg/mL tert butyl alcohol; 1000 µg/mL acrolein, isopropanol, isobutanol; 5000 µg/mL 1,4-dioxane, 1-propanol, n-butanol, ethanol	CAL Stock Standard	100 µg/mL all compounds except as follows: 250 µg/mL acetonitrile,; 500 µg/mL tert butyl alcohol; 1000 µg/mL acrolein, isopropanol, isobutanol; 5000 µg/mL 1,4-dioxane, 1-propanol, n-butanol, ethanol	1250 µL of 2000 µg/mL 502.2 Calibration Gases Mix 1250 µL of 2000 µg/mL 502.2 Cal 2000 Megamix 238 µL of 10,500 µg/mL Vinyl Acetate -Cal 500 µL of 5000 µg/mL Calibration KetoneMix 1250 µL of 2000 µg/mL Pace GB Custom Mix #3 1250 µL of 20000 µg/mL Acrolein -Cal 1250 µL of 2000 µg/mL 2-Chloroethylvinyl ether Diluted into methanol Surrogates are added by the instrument during aqueous and low level soil calibration events.	25 mL
100 µg/mL Calibration Std. 250 µg/mL acetonitrile; 500 µg/mL tert butyl alcohol; 1000 µg/mL acrolein, isopropanol, isobutanol; 5000 µg/mL 1,4-dioxane, 1-propanol, n-butanol, ethanol	ICV Stock Standard	100 µg/mL all compounds except as follows: 250 µg/mL acetonitrile,; 500 µg/mL tert butyl alcohol; 1000 µg/mL, isopropanol, isobutanol; 5000 µg/mL 1,4-dioxane, 1-propanol, n-butanol, ethanol	1250 µL of 2000 µg/mL 502.2 ICV Gases Mix 1250 µL of 2000 µg/mL Megamix – ICV 1250 µL of 2000 µg/mL Ketones ICV 1250 µL of 2000 µg/mL Custom – ICV Diluted into methanol	25 mL
MeOH Level 1 Calibration Standard (MeOH Curve Only)	CAL1 (MeOH Curve Only)	0.40µg/L all compounds except as follows: 1.0 µg/L acetonitrile; 2.0 µg/L tert butyl alcohol; 4.0 µg/L acrolein, isopropanol, isobutanol; 20 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Methanol curve only dilute: 2.0 µL 100 µg/mL CAL Stock Standard and 1 µL 250 µg/mL Surrogate Standard into 490 mL reverse osmosis water and 10 mL methanol	500 mL
Water Level 1 Calibration Standard MeOH Level 2 Calibration Standard	CAL1 (Water) CAL2 (MeOH)	1.0µg/L all compounds except as follows: 2.5 µg/L acetonitrile; 5.0 µg/L tert butyl alcohol; 10 µg/L acrolein, isopropanol, isobutanol; 50 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Water Curve: Dilute 5 µL of 100 µg/mL CAL Stock Standard into 500 mL reverse osmosis water. If for a methanol curve dilute: 5 µL 100 µg/mL CAL Stock Standard and 2 µL 250 µg/mL Surrogate Standard into 490 mL reverse osmosis water and 10 mL methanol.	500 mL
Water Level 2	CAL2	5.0 µg/L all compounds	Water Curve:	50 mL

Standard	Acronym	Concentration of Intermediate	Reagents Used	Final Volume
Calibration Standard MeOH Level 3 Calibration Standard	(Water) CAL3 (MeOH)	except as follows: 12.5 µg/L acetonitrile; 25 µg/L tert butyl alcohol; 50 µg/L acrolein, isopropanol, isobutanol; 250 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Dilute 2.5 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 2.5 µL 100 µg/mL CAL Stock Standard and 1 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 1 mL methanol.	
Water Level 3 Calibration Standard MeOH Level 4 Calibration Standard	CAL3 (Water) CAL4 (MeOH)	20 µg/L all compounds except as follows: 50 µg/L acetonitrile,; 100 µg/L tert butyl alcohol; 200 µg/L acrolein, isopropanol, isobutanol; 1000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Water Curve: Dilute 10 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 10 µL 100 µg/mL CAL Stock Standard and 4 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 990 µL methanol.	50 mL
Water Level 4 Calibration Standard MeOH Level 5 Calibration Standard	CAL4 (Water) CAL5 (MeOH)	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Water Curve: Dilute 25 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 25 µL 100 µg/mL CAL Stock Standard and 10 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 960 µL methanol.	50 mL
Water Level 5 Calibration Standard MeOH Level 6 Calibration Standard	CAL5 (Water) CAL6 (MeOH)	100 µg/L all compounds except as follows: 250 µg/L acetonitrile; 500 µg/L tert butyl alcohol; 1000 µg/L acrolein, isopropanol, isobutanol; 5000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Water Curve: Dilute 50 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 50 µL 100 µg/mL CAL Stock Standard and 20 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 930 µL methanol.	50 mL
Water Level 6 Calibration Standard MeOH Level 7 Calibration Standard	CAL6 (Water) CAL7 (MeOH)	200 µg/L all compounds except as follows: 500 µg/L acetonitrile; 1000 µg/L tert butyl alcohol; 2000 µg/L acrolein, isopropanol, isobutanol; 10000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Water Curve: Dilute 100 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 100 µL 100 µg/mL CAL Stock Standard and 40 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 860 µL methanol.	50 mL
Water Level 7 Calibration Standard (Water Curve only)	CAL7 (Water Curve only)	300 µg/L all compounds except as follows: 750 µg/L acetonitrile; 1500 µg/L tert butyl alcohol; 3000 µg/L acrolein, isopropanol, isobutanol; 15000 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Water Curve Only: Dilute 150 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water.	50 mL

Standard	Acronym	Concentration of Intermediate	Reagents Used	Final Volume
*Optional Water Level3 Calibration Standard * If this standard is made for a water Curve, all subsequent Water Level # will increment by 1 (i.e. 300µg/L will now be CAL8)	CAL3 (Water Curve only) *Optional	10 µg/L all compounds except as follows: 25 µg/L acetonitrile; 50 µg/L tert butyl alcohol; 100 µg/L acrolein, isopropanol, isobutanol; 500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol.	Water Curve: Dilute 5 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water.	50 mL
Independent Calibration Verification Standard	ICV050	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Water Curve: Dilute 25 µL of 100 µg/mL ICV Stock Standard and 25 µL Reactive Mix – ICV into 50 mL reverse osmosis water. If for a methanol curve dilute: 25 µL 100 µg/mL ICV Stock Standard, 25 µL Reactive Mix – ICV and 10 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 940 µL methanol.	50 mL
Calibration Verification Standard	CCV050	50 µg/L all compounds except as follows: 125 µg/L acetonitrile; 250 µg/L tert butyl alcohol; 500 µg/L acrolein, isopropanol, isobutanol; 2500 µg/L 1,4-dioxane, 1-propanol, n-butanol, ethanol	Water Curve: Dilute 25 µL of 100 µg/mL CAL Stock Standard into 50 mL reverse osmosis water. If for a methanol curve dilute: 25 µL 100 µg/mL CAL Stock Standard and 10 µL 250 µg/mL Surrogate Standard into 49 mL reverse osmosis water and 960 µL methanol.	50 mL
Matrix Spike/Lab Control Spike Stock Solution - TCL 4.1 List for Water and Low Level Soil Samples	MS/LCS TCL 4.1 List Stock Solution for Water and Low Level Soil Samples	100 µg/mL for all compounds	1250 µL of 2000 µg/mL CLP 4.1Mega Mix 1250 µL of 2000 µg/mL 502.2 Gases Mix #1 Dilute into methanol.	25 mL
Matrix Spike/Lab Control Spike Stock Solution - TCL 4.1 List for Methanol Preserved Soil Samples	MS/LCS TCL 4.1 List Stock Solution for Methanol Preserved Soil Samples	500 µg/mL for all compounds	2500 µL of 2000 µg/mL CLP 4.1Mega Mix 2500 µL of 2000 µg/mL 502.2 Gases Mix #1 Dilute into methanol.	10 mL
Matrix Spike/Lab Control Spike Stock Solution - Full List *	MS/LCS Stock Solution – Full List	100 µg/mL all compounds except as follows: 250 µg/mL acetonitrile; 500 µg/mL tert butyl alcohol; 1000 µg/mL	1250 µL of 2000 µg/mL 502.2 ICV Gases Mix 1250 µL of 2000 µg/mL Megamix – ICV 1250 µL of 2000 µg/mL Ketones ICV 1250 µL of 2000 µg/mL Custom – ICV Diluted into methanol	25 mL

Standard	Acronym	Concentration of Intermediate	Reagents Used	Final Volume
		isopropanol, isobutanol; 5000 µg/mL 1,4-dioxane, 1-propanol, n-butanol, ethanol		
MS/MSD – LCS/LCSD Spike for Water Samples	MS/MSD LCS/LCSD	50 µg/L for most compounds, Various for others.	Add 21 µL of the appropriate Matrix Spike/ Lab Control Spike Solution to 42 mL of sample for MS/MSD, or 42 mL of reagent water for LCS/LCSD	42 mL
MS/MSD – LCS/LCSD Spike for 624 Water Samples	MS/MSD LCS/LCSD	20 µg/L for most compounds, Various for others	Add 8.4 µL of the appropriate Matrix Spike / Lab Control Spike Solution to 42 mL of sample for MS/MSD or 42 mL of reagent water for LCS/LCSD.	42 mL
MS/MSD – LCS/LCSD Spike for Low Level Soil Samples	MS/MSD LCS/LCSD	50 µg/kg for most compounds, Various for others.	Add 2.5 µL of the appropriate Matrix Spike/ Lab Control Spike Solution to 5.0 g of sample containing 5 mL of reagent water for MS/MSD, or 5.0 g of Ottawa sand containing 5 mL of reagent water for LCS/LCSD	5 mL
MS/MSD – LCS/LCSD Spike for Methanol Preserved Soil Samples Standard List	MS/MSD LCS/LCSD	2500 µg/kg for most compounds, Various for others.	Add 50 µL of the Standard List Matrix Spike/ Lab Control Spike Solution to 10 g of sample containing 10 mL of methanol for MS/MSD, amount of Spike Solution is adjusted according to the initial methanol volume; or 10 g of Ottawa sand containing 10 mL of methanol for LCS/LCSD	10 mL
MS/MSD – LCS/LCSD Spike for Methanol Preserved Soil Samples Full List	MS/MSD LCS/LCSD	2500 µg/kg for most compounds, Various for others.	Add 250 µL of the Full List Matrix Spike/ Lab Control Spike Solution to 10 g of sample containing 10 mL of methanol for MS/MSD, amount of Spike Solution is adjusted according to the initial methanol volume; or 10 g of Ottawa sand containing 10 mL of methanol for LCS/LCSD	10 mL

*Samples to be analyzed by EPA 624 originating in the State of South Carolina must contain all analytes of interest in the LCS, MS, and MSD.

11. Calibration and Standardization

11.1. Tune Verification

The mass spectrometer tune status must be verified prior to initial calibration and at the beginning of each analytical sequence. If the current tune status does not meet the ion ratio criteria in the method (see section 11.2), follow the equipment manufacturers' instructions for re-tuning the mass spectrometer. The tune status must be verified after the tuning procedures.

11.2. Initial Calibration (ICAL)

11.2.1. Analysis of Standards

An initial calibration curve using a minimum of five points is analyzed prior to analyzing client samples. The lowest concentration must be at or below the equivalence of the standard reporting limit. The lowest calibration point reflects the practical quantitation limit for that compound, a level below which all reported results must be qualified as estimated values. Refer to table 11.1 for compound concentrations.

An analyte must be present and calibration curve in control in order to be reported on the target analyte list. Analytes identified by mass spectral match but not present and in control

in the calibration table may be reported as Tentatively Identified Compounds (TICs). Guidelines for identification are listed in Section 12.6.3. Results for these TICs should be reported only on a present/absent basis. However, quantitative results may be reported provided they are qualified as estimated values.

Table 11.1: Calibration standard compound concentrations

Analyte	PQL water µg/L	PQL soil µg/kg	PQL 5035 soil µg/Kg	Cal1 MeOH curve only µg/L	Cal2 MeOH Cal1 water µg/L	Cal3 MeOH Cal2 water µg/L	Cal4 MeOH Cal3 water µg/L	Cal5 MeOH Cal4 water µg/L	Cal6 MeOH Cal5water µg/L	Cal7 MeOH Cal6 water µg/L	Cal7 water Curve only µg/L	* Optional Cal3 water Curve only µg/L
1,1-Dichloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,1-Dichloroethene	1	50	5	-	1	5	20	50	100	200	300	10
1,1-Dichloropropene	1	50	5	-	1	5	20	50	100	200	300	10
1,1,1-Trichloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,1,2-Trichloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,1,2-Trichloro-1,1,2trifluoethane	5	50	5	-	1	5	20	50	100	200	300	10
1,1,1,2-Tetrachloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,1,2,2-Tetrachloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,2,4-Trichlorobenzene	5	250	5	-	1	5	20	50	100	200	300	10
1,2-Dichlorobenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,2-Dibromo-3-chloropropane	5	250	5	-	1	5	20	50	100	200	300	10
1,2-Dichloroethane	1	50	5	-	1	5	20	50	100	200	300	10
1,2-Dibromoethane	1	50	5	-	1	5	20	50	100	200	300	10
1,2-Dichloropropane	1	50	5	-	1	5	20	50	100	200	300	10
1,2-Dichloroethene (Total)	2	100	10	-	2	10	40	100	200	400	600	20
1,2,3-Trimethylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,2,4-Trimethylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,2,3-Trichlorobenzene	5	50	5	-	1	5	20	50	100	200	300	10
1,2,3-Trichloropropane	1	50	5	-	1	5	20	50	100	200	300	10
1,3-Dichlorobenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,3-Dichloropropane	1	50	5	-	1	5	20	50	100	200	300	10
1,3,5-Trimethylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,4-Dichlorobenzene	1	50	5	-	1	5	20	50	100	200	300	10
1,4-Dioxane (p-Dioxane)	250	12500	250	-	50	250	1000	2500	5000	10000	15000	500
1-Methylnaphthalene	5	250	5	-	1	5	20	50	100	200	300	10
2,2-Dichloropropane	1	50	5	-	1	5	20	50	100	200	300	10
2,3-Dichloropropene	1	50	5	-	1	5	20	50	100	200	300	10
2-Butanone (MEK)	20	250	20	-	1	5	20	50	100	200	300	10
2-Chlorotoluene	1	50	5	-	1	5	20	50	100	200	300	10
2-Chloroethylvinyl ether	5	250	10	-	1	5	20	50	100	200	300	10
2-Hexanone	5	250	5	-	1	5	20	50	100	200	300	10
2-Methylnaphthalene	5	250	5	-	1	5	20	50	100	200	300	10
2-Propanol	250	12500	50	-	10	50	200	500	1000	2000	3000	100
Allyl chloride	5	250	5	-	1	5	20	50	100	200	300	10
4-Chlorotoluene	1	50	5	-	1	5	20	50	100	200	300	10
TOTAL BTEX	1	300	30	-	1	5	20	50	100	200	300	10
Carbon disulfide	5	50	5	-	1	5	20	50	100	200	300	10
Ethanol	500	NA	500	-	50	250	1000	2500	5000	10000	15000	500
Acetone	20	250	20	-	1	5	20	50	100	200	300	10
Acrolein	20	2500	50	-	10	50	200	500	1000	2000	3000	100
Acetonitrile	20	250	12.5	-	2.5	12.5	50	125	250	500	750	25
Acrylonitrile	5	250	5	-	1	5	20	50	100	200	300	10

Analyte	PQL water µg/L	PQL soil µg/kg	PQL 5035 soil µg/Kg	Cal1 MeOH curve only µg/L	Cal2 MeOH Cal1 water µg/L	Cal3 MeOH Cal2 water µg/L	Cal4 MeOH Cal3 water µg/L	Cal5 MeOH Cal4 water µg/L	Cal6 MeOH Cal5water µg/L	Cal7 MeOH Cal6 water µg/L	Cal7 water Curve only µg/L	* Optional Cal3 water Curve only µg/L
Bromochloromethane	1	50	5	-	1	5	20	50	100	200	300	10
Benzene	1	20	5	0.4	1	5	20	50	100	200	300	10
Bromobenzene	1	50	5	-	1	5	20	50	100	200	300	10
Bromodichloromethane	1	50	5	-	1	5	20	50	100	200	300	10
Bromomethane	5	250	10	-	1	5	20	50	100	200	300	10
Bromoform	1	50	5	-	1	5	20	50	100	200	300	10
cis-1,2-Dichloroethene	1	50	5	-	1	5	20	50	100	200	300	10
cis-1,3-Dichloropropene	1	50	5	-	1	5	20	50	100	200	300	10
cis-1,4-Dichloro-2-butene	5	250	10	-	1	5	20	50	100	200	300	10
Carbon tetrachloride	1	50	5	-	1	5	20	50	100	200	300	10
Cyclohexane	5	250	5	-	1	5	20	50	100	200	300	10
Chlorobenzene	1	50	5	-	1	5	20	50	100	200	300	10
Chloroethane	1	250	5	-	1	5	20	50	100	200	300	10
Chloroform	5	250	5	-	1	5	20	50	100	200	300	10
Chloromethane	1	50	5	-	1	5	20	50	100	200	300	10
Dibromochloromethane	1	50	5	-	1	5	20	50	100	200	300	10
Dichlorofluoromethane	1	50	5	-	1	5	20	50	100	200	300	10
Diethyl ether (Ethyl ether)	5	50	5	-	1	5	20	50	100	200	300	10
Dichlorodifluoromethane	1	50	5	-	1	5	20	50	100	200	300	10
Diisopropyl ether	1	50	5	-	1	5	20	50	100	200	300	10
Dibromomethane	1	50	5	-	1	5	20	50	100	200	300	10
Ethylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
Ethyl-tert-butyl ether	5	250	5	-	1	5	20	50	100	200	300	10
Hexachloro-1,3-butadiene	5	50	5	-	1	5	20	50	100	200	300	10
Hexachloroethane	5	250	5	-	1	5	20	50	100	200	300	10
Iodomethane	5	250	5	-	1	5	20	50	100	200	300	10
Isopropylbenzene (Cumene)	1	50	5	-	1	5	20	50	100	200	300	10
Isopropyl acetate	5	250	5	-	1	5	20	50	100	200	300	10
Isobutanol	50	2500	50	-	10	50	200	500	1000	2000	3000	100
Methyl acetate	10	250	20	-	1	5	20	50	100	200	300	10
Methylene Chloride	1	50	5	-	1	5	20	50	100	200	300	10
Methylcyclohexane	5	250	5	-	1	5	20	50	100	200	300	10
Methyl-tert-butyl ether	1	50	5	-	1	5	20	50	100	200	300	10
4-Methyl-2-pentanone	5	250	5	-	1	5	20	50	100	200	300	10
m&p-Xylene	2	100	10	-	2	10	40	100	200	400	600	20
Naphthalene	5	250	5	-	1	5	20	50	100	200	300	10
n-Butanol	250	12500	250	-	50	250	1000	2500	5000	10000	15000	500
n-Butylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
n-Heptane	5	250	5	-	1	5	20	50	100	200	300	10
n-Hexane	5	250	5	-	1	5	20	50	100	200	300	10
n-Propylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
n-Propanol	250	12500	250	-	50	250	1000	2500	5000	10000	15000	500
o-Xylene	1	50	5	-	1	5	20	50	100	200	300	10
p-Isopropyltoluene	1	50	5	-	1	5	20	50	100	200	300	10
sec-Butlybenzene	5	50	5	-	1	5	20	50	100	200	300	10
Styrene	1	50	5	-	1	5	20	50	100	200	300	10
trans-1,2-Dichloroethene	1	50	5	-	1	5	20	50	100	200	300	10
trans-1,3-Dichloropropene	1	50	5	-	1	5	20	50	100	200	300	10

Analyte	PQL water µg/L	PQL soil µg/kg	PQL 5035 soil µg/Kg	Cal1 MeOH curve only µg/L	Cal2 MeOH Cal1 water µg/L	Cal3 MeOH Cal2 water µg/L	Cal4 MeOH Cal3 water µg/L	Cal5 MeOH Cal4 water µg/L	Cal6 MeOH Cal5water µg/L	Cal7 MeOH Cal6 water µg/L	Cal7 water Curve only µg/L	* Optional Cal3 water Curve only µg/L
trans-1,4-Dichloro-2-butene	5	250	5	-	1	5	20	50	100	200	300	10
tert-Amyl-methyl ether	1	250	5	-	1	5	20	50	100	200	300	10
tert-Butyl Alcohol	25	1250	50	-	5	25	100	250	500	1000	1500	50
Tetrachloroethene	1	50	5	-	1	5	20	50	100	200	300	10
Tetrahydrofuran	5	250	10	-	1	5	20	50	100	200	300	10
Toluene	1	50	5	-	1	5	20	50	100	200	300	10
Trichloroethene	1	50	5	-	1	5	20	50	100	200	300	10
Trichlorofluoromethane	1	50	5	-	1	5	20	50	100	200	300	10
tert-Butylbenzene	1	50	5	-	1	5	20	50	100	200	300	10
Xylene (Total)	3	150	15	-	3	15	60	150	300	600	900	30
Vinyl acetate	5	250	5	-	1	5	20	50	100	200	300	10
Vinyl chloride	1	50	5	-	1	5	20	50	100	200	300	10

*** If the Optional Cal 3 point is made for the Water Curve all subsequent Cal levels will increase by 1 (i.e. 300µg/L is now CAL8)**

11.2.2. Calibration Response Factors

Response factors (RF) establish the relationship of the instruments response in comparison with the concentration of any given analyte. The RF includes the concentration and response of the internal standard as well. By relating the IS concentration and response in an inverse manner, the target analyte concentration is adjusted to account for drift in the instrument on a per injection basis. As instrument response increases as indicated by the response of the internal standard, the concentration of the target is mathematically decreased, and vice versa.

To calculate the RF for any given calibration standard (or calibration verification standard), tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. Response factors are calculated using the following equation.

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

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_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L).

Most, if not all modern chromatography data systems are capable of calculating this factor and using it to quantify analyte concentrations. The 8260B method has minimum requirements that these response factors must meet in order to be considered valid. The method uses a subset of the target analyte list to evaluate the performance of the system.

These compounds are referred to as the System Performance Check Compounds or the SPCCs. The SPCCs serve as an indicator of instrument sensitivity and, by meeting a minimum value, ensure that the laboratory has adequate sensitivity to analyze and reliably report data for environmental samples.

11.2.3. Calibration Curve Fit

The calibration curve is a representation of the relationship of the instrument response and analyte concentration. The curve is used to quantitate the concentration of an unknown based on its response and this known relationship. The curve is produced in several ways depending on the nature of the "goodness of fit".

Average Response Factor (ARF): The average response factor is determined by averaging the response factors calculated for each calibration level for each target analyte. The average RF can be used to calculate the concentration of target analytes in samples provided the criteria are met for consistency in the RFs for any given analyte. An average response factor is the default curve fitting option for calibrations. It is in the most basic sense, a linear regression that is forced through zero at the origin. Because of its simplicity and the interception of the y axis at the origin, this is the preferred technique for curve fitting. A calculation of the percent relative standard deviation (%RSD) is used to determine the acceptability of the use of the ARF (see Table 11.2).

The % RSD is calculated as follows: %RSD = SD*100 / ARF

Where: SD = Standard deviation of the averaged RFs for a given compound

The average response factor is also used to diagnose the integrity of the chromatography system as it relates to calibration linearity. The ***Calibration Check Compounds (CCCs)*** are a subset of the target analyte list that must meet specific criteria (see Table 11.2) for the calibration to be acceptable. For the CCCs, the %RSD for each is compared to the method criteria. If that of any CCC exceeds the criteria, the system needs to be inspected for potential sources of errors and recalibrated.

Linear Regression: The linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of y=ax+b where "a" is the slope of the line and "b" is the y intercept. In order to use this curve fit technique, a minimum of 5 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument is linear in nature but does not necessarily intercept the y-axis at the origin. However, because the linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. A calculation of the correlation coefficient "r" is used to determine the acceptability of a linear regressed curve (see Table 11.2)

Non-linear Regression: The non-linear regression calibration curve is derived from a least squares regression analysis of the calibration points. A calibration curve based on this technique will have the format of $y= ax^2+bx+c$. In order to use this curve fit technique, a minimum of 6 calibration points must be available and the origin cannot be included as one of the points. This technique works well for calibrations where the response of the instrument gradually decreases with increasing concentrations. Using this technique, an

analyst may be able to generate calibration curves with correlation coefficients very close or equivalent to 1.000. However, because the non-linear regression is not forced through the origin, very low levels of contaminants below the response of the lowest calibration point may generate erroneous reportable results. Likewise, high levels of contamination may not be able to be calculated due to regression equations with multiple intercepts of either axis on the calibration plot.

Note: The State of South Carolina does not allow the use of Non-linear regression for compliance samples.

Analytes that have poor purging efficiency or are problematic compounds may require the use of Non-linear regression curves. These may include: Bromomethane, 1-Propanol, Acrolein (2-propenal), n-Butanol, 2-Butanone, Carbon Disulfide, Hexachloroethane, and 1,2-Dibromo-3-chloropropane (DBCP)

Refer to section 11.2.3 for curve fit criteria. Either the low or high calibration points may be dropped to meet linearity criteria provided the laboratory meets the minimum 5 calibration point requirements. Points within the center of the curve may not be dropped unless an obvious problem is discovered and documented. The point must be dropped in its entirety and reanalyzed. Re-analysis should be within the same 12-hour time window and must occur within 8 hours of the original analysis.

11.3. Calibration Verification

11.3.1. Second Source Verification (SCV)

In addition to meeting the linearity criteria, any new calibration curve must be assessed for accuracy in the values generated. Accuracy is a function of both the "fit" of the curve to the points used and the accuracy of the standards used to generate the calibration points. By meeting the fit criteria, the accuracy relative to the goodness of fit is addressed. However, because all calibration points are from the same source, it is possible that the calibration points may meet linearity criteria but not be accurately made in terms of their true value.

Therefore, to assess the accuracy relative to the purity of the standards, a single standard from a secondary source must be analyzed and the results obtained must be assessed relative to the known true value. This step is referred to as ***Secondary Source Verification*** or, alternatively as ***Initial Calibration Verification***. This secondary source must be from an alternative vendor or, in the event an alternative vendor is not available, from a different lot from the same vendor. The accuracy of the standard is assessed as a percent difference from the true value according to the following equation:

$$\% \text{ Difference} = [\text{Result}_{SCV} - \text{TrueValue}_{SCV}] / \text{TrueValue}_{SCV} * 100$$

See Tables 10.6 and 10.7 for details on the preparation of this standard. See Table 11.2 for control criteria.

11.3.2. Continuing Calibration Verification (CCV)

As part of the analytical process, the instrumentation must be checked periodically to determine if the response has changed significantly since the initial calibration was established. This verification process is known as ***Continuing Calibration Verification***. The validity of the initial calibration is checked at the beginning of every analytical

sequence and every 12 hours thereafter for as long as the instrument is analyzing samples and is accomplished by analyzing a midpoint calibration standard (CCV).

The values obtained from the analysis of the CCV are compared to the true values and a percent change calculated. The percent change must meet the method specified criteria for the analysis to proceed for an additional 12 hours.

The actual determination of change in instrument response is based on the type of curve fit used for each analyte. Calibration curves based on an average response factor are assessed based on the percent difference of the RF calculated for the CCV from the average RF established in the initial calibration. Calibration curves based on a linear or non-linear regression are assessed based on the percent drift of the calculated result from the known true value of the standard. The equations for these calculations are as follows:

% Difference: $[RF_{CCV} - AvgRF_{CAL}] / AvgRF_{CALl} \times 100$

% Drift: $[Result_{CCV} - TrueValue_{CCV}] / TrueValue_{CCV} \times 100$

Table 11.2 – Calibration Acceptance and Verification Criteria

Calibration Metric	Parameter / Frequency	Criteria	Comments
Calibration Curve Fit	Average Response Factor Linear Regression Non-linear Regression	%RSD ≤ 15% r ≥ 0.99 COD ≥ 0.99	If not met, try linear regression fit If not met, try non-linear regression fit If not met, remake standards and recalibrate
System Performance Check Compounds (SPCCs)	Chloromethane 1,1-Dichloroethane Bromoform Chlorobenzene 1,1,2,2-Tetrachloroethane	Avg RF ≥ 0.10 Avg RF ≥ 0.10 Avg RF ≥ 0.10 Avg RF ≥ 0.30 Avg RF ≥ 0.30	Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, poor purging efficiency, and active sites in the column or chromatographic system.
Calibration Check Compounds (CCCs)	1,1-Dichloroethene Toluene Chloroform Ethylbenzene 1,2-Dichloropropane Vinyl Chloride	%RSD < 30%	%RSD for the calibration check compounds (CCC's) must be ≤30% regardless of curve fit used. If the CCCs are not included on a list of analytes for a project, and therefore not included in the calibration standards, then all compounds of interest must meet a ≤15% RSD criterion.
Second Source Verification Standard	Immediately after each initial calibration	% Diff ±30%	Acceptance criteria are ±30% for all analytes, with allowances for 5% of compounds @ ±40%. See ALL_Q_025_Rev.1
Continuing Calibration Verification	Prior to the analysis of any samples and every 12 hours thereafter		If the requirements for continuing calibration are not met, these corrective actions must be taken prior to reanalysis of standards. Only two injections of the same standard are permitted back to back.
	SPCCs	Must meet response criteria listed above	
	Internal Standard RT Internal Standard Response	RT ± 30 sec 50 – 200%	Use midpoint calibration standard as reference Use midpoint calibration standard as reference
	CCCs	RF ± 20% Diff. Result ± 20% Drift	Use for Avg RF calibration curves Use for linear and non-linear calibration curves Additional client specific requirements for the analysis of contract samples requires that BTEX, PAH, Oxygenates, and surrogate compounds also be considered CCCs and must meet the 20% CCV criterion.
	Non-CCC Targets	RF ± 50% Diff.* Result ±50% Drift	Some programs may require control over non-CCC target analytes. In the absence of specified criteria, use those listed *State of South Carolina requires non-CCC Compounds to meet ±30% Drift. Please Note: Analytes that have poor purging efficiency or are problematic compounds may require the use ±50% Drift. These may include: Bromomethane, 1-Propanol, Acrolein (2-propenal), n-Butanol, 2-Butanone, Carbon Disulfide, Hexachloroethane, and 1,2-Dibromo-3-chloropropane (DBCP)

11.4. Calibration Corrective Actions

11.4.1. Calibration Linearity Problems

11.4.1.1. Check instrumentation/equipment condition.

11.4.1.2. Enter maintenance in instrument maintenance logbook.

11.4.1.3. Perform another initial calibration.

11.4.1.4. No data can be reported.

11.4.1.5. Generate on Non-Conformance Memo.

11.4.2. Secondary Verification Problems

11.4.2.1. Check instrumentation/equipment condition.

11.4.2.2. Enter maintenance in instrument maintenance logbook.

11.4.2.3. Perform another initial calibration.

11.4.2.4. No data can be reported.

11.4.2.5. Generate on Non-Conformance Memo

11.4.3. Continuing Verification Problems

11.4.3.1. Reanalyze the original CCV standard to determine instrument consistency.

11.4.3.2. Prepare and analyze a new CCV standard to determine preparation consistency / standard integrity.

11.4.3.3. Document instrument maintenance

11.4.3.4. Reanalyze CCV standard to determine if maintenance was effective in restoring performance.

11.4.3.5. Complete recalibration of instrument.

11.4.3.6. If samples were analyzed in spite of verification failures, note the following exceptions for addressing those results. Deviations from this requirement must be noted on the injection log with a thorough explanation for the deviation from policy.

Exceptions: If calibration verification is above the upper control limit, samples non-detected for those analytes may be reported without reanalysis.

12. Procedure

12.1. Purge-Trap GC/MS System Preparation

12.1.1. Operating Parameters

Configure the GC/MS system to match the following operating parameters based on instrument configuration. The parameters themselves are saved as a method on the chromatography data system. By loading the last method used, the instrument will auto-configure to match the parameters from the last time the system was operated under that method. Verify that the settings in the software match the appropriate configuration.

Table 12.1 –Instruments and Operating Parameters

Component	**Settings and Consumables**	
Gas Chromatograph	**Column**: J&W Scientific DB-624 Capillary Column, 20m x 0.18 mm, i.d. 1.0 µm **Inlet Liner:** Restek 4 mm Single Gooseneck Injection Port Liners **Inlet Seal:** Restek Gold Plated inlet seal **Column Ferrules:** Restek 04.mm Vespel/Graphite ferrules	Pressure / Flow: 0.5-1.0 mL / min Initial Temperature: 40°C Initial Time: 3 min Final Temperature: 8°C / min to 110°C 0 min hold 20°C / min to 220°C 1 min hold Final Time: 18.25 min Injector Temperature: 220°C Detector Temperature: 240°C
Mass Spectrometer	Tune File: Named to date of tune	
Purge & Trap Concentrator	Prepurge: NO Preheat: 40°C Sample: 20°C Purge: 10 min Dry Purge: NO Desorb Preheat: 245°C Desorb: 250°C	Standby: - Bake: 270°C for 5-7 min BGB: OFF Valve: 150°C Line: 150°C Mount: N/A Transfer Line Temp: 150°C
Autosampler	Syringe Flushes: 2 Sparge Tube Flushes: 2	

12.2. Tune Verification

At the beginning of each analytical sequence, prior to the analysis of any standards or samples, the mass spectrometer tune conditions must be verified. This is done by analyzing a standard containing bromofluorobenzene (refer to table 10.2). The tune verification standard can be combined with the CCV standard provided that the amount of BFB introduced into the system meets the criteria in Section 12.2.

After the analysis of this standard, the mass spectrum of BFB must be evaluated against the following criteria.

Mass (m/z)	Ion Abundance criteria
50	15.00-40.00% of m/z 95
75	30.00-60.00% of m/z 95
95	Base peak, 100% relative abundance
96	5.00-9.00% of m/z 95
173	<2.00% of m/z 174
174	50.00-100.00% of m/z 95
175	5.00-9.00% of m/z 174
176	95.00-101.00% of m/z 174
177	5.00-9.00% of m/z 176

To evaluate the tune spectra, following the operating instructions for the chromatography data system to access the data file and obtain mass spectra for bromofluorobenzene. If the software has a program or macro for automatically selecting the spectra and evaluating the response ratios, use this option. Additionally, see Attachment III and Attachment IV on the proper techniques for evaluation of the tune file. Otherwise, the spectra must be obtained in one the following manners, in the listed order.

1. Using an average of three scans, centered on the apex of the peak; or,

2. Using an average of all scans across the width of the peak, taken at half height; or,

3. Using an average of all scans taken across the width of the peak from baseline to baseline.

A background scan taken immediately before but not including the peak must be subtracted.

Once obtained, evaluate the ion ratios against the criteria listed above. If the ratios meet the criteria, then analysis may proceed for 12 hours. The window for analysis is 12 hours from the injection date / time for the BFB tune verification. After that, the tune must be verified again to establish a new analytical window. The same Ion Abundance Criteria used for the BFB tune coupled with the initial calibration must be used for all subsequent analyses associated with that initial calibration.

If the ratios do not meet the criteria, refer to the following corrective actions to address the problem:

1. Retune the mass spectrometer following the equipment manufacturers' instructions. The tune status must be verified after the tuning procedures.
2. If this fails, change filament and retune.
3. If this fails, take down the mass spectrometer and clean the instrument.

12.3. Calibration Verification

After the instrument tune conditions are verified and the system meets tune criteria, the instrument must undergo calibration verification. If it has already been determined that the instrument needs to be recalibrated, follow the procedures listed in section 11.2 (Analysis of Standards). Otherwise, analyze a Continuing Calibration Verification Standard to determine the current calibration status.

If the CCV meets control criteria, the system is deemed to be in control and analysis of samples may commence. If the CCV does not meet control criteria, follow the corrective action procedures listed section 11.4.3 (Continuing Verification Problems). If the tune verification has been combined with the CCV, the 12 hour analysis window begins from the analysis date / time of the CCV.

Note: In situations where the instrument will run unattended (i.e. overnight), the analyst may load sequential CCVs in anticipation of that the first in the series may fail due to carry over from a previous sample. If so, the CCV must be evaluated according to the protocol set forth in the Quality Assurance Manual within Section 6 – Equipment and Measurement Traceability.

12.4. Operation of the Software Systems

12.4.1. Epic Pro

12.4.1.1. **Make Q-Batch**

12.4.1.1.1. Batching -> New Batch -> Queue = MSV
12.4.1.1.2. Click Empty Batch icon on taskbar
12.4.1.1.3. Highlight QC Rule -> F9 -> type MSV
12.4.1.1.4. Select appropriate QC Rule (i.e. MSV water) – Select OK – F10 to save
12.4.1.1.5. Record Q Batch #

12.4.1.2. **Create Standards**

12.4.1.2.1. System -> Utility -> Clone Standard by Event
12.4.1.2.2. Select Event (111 = MeOH soil curve, 115 = Water/LLsoil curve) Select OK
12.4.1.2.3. Double Click on standard event
12.4.1.2.4. Review Standard composed of – Find/Replace if necessary
12.4.1.2.5. Update expiration date to 7 days from creation – F10 to Save
12.4.1.2.6. Operations -> Standard Log -> Enter – Record Standard #'s

12.4.2. Chemstation

12.4.2.1. **Create Chemstation methods**

12.4.2.1.1. Tune MS, Save Tune file as date (i.e. 072513.u)
12.4.2.1.2. Update both DBFB and Curve method to use new tune file
12.4.2.1.3. Save Curve method as date (i.e. W072513.m)

12.4.2.2. **Set up Sequence**

12.4.2.2.1. Load pre-existing curve sequence if available
12.4.2.2.2. Change old method to the new method & copy through all files

(DBFB remains the same)

12.4.2.2.3. Change Q-Batch # in BFB, Curve and ICV files

12.4.2.3. **Start Analysis**

12.4.2.3.1. Run minimum of 2 BFB injections to ensure the tune is optimized

12.4.2.3.2. Retune or adjust as needed, repeat 2 more BFB

12.4.2.3.3. Analyze a 2 blanks to verify the system is clean and IS areas within range

12.4.2.3.4. First IS, pentafluorobenzene should be between 300,000 – 550,000 area counts

12.4.2.3.5. Raise or lower EM as necessary – You ***Must*** reanalyze BFB if voltage was adjusted

12.4.2.3.6. Reanalyze blanks to ensure correct voltage and proceed w/ analysis of curve

12.4.3. Target

12.4.3.1. **Create Method**

12.4.3.1.1. Rename existing method to new name matching Chemstation method (i.e. W072513.m)

Note: if other data in Directory was processed w/ old method a copy of that method must remain in directory as well.

12.4.3.1.2. To avoid excessive file size, Audit trail in method should be reset at a minimum of annually

The ***ONLY*** time an audit trail may be rest is prior to calibrating the instrument.

Note: The Audit trail will remain intact in previous day's folder.

Double click into method folder, highlight the .audit file and delete

12.4.3.2. **Edit Method**

12.4.3.2.1. Security -> Method unlocked

12.4.3.2.2. Global -> Calibration – Click "update Curve Parameters" to averaged

12.4.3.2.3. File -> Zero Calibration

12.4.3.2.4. Compound -> Edit Compound -> Calibration

12.4.3.2.4.1. Review all analytes to ensure all necessary points are enabled

12.4.3.2.4.2. Are any 300 points dropped? If so, mark them enabled and make note of these to change the "Max Compound Amount Limit" after the curve has been run.

12.4.3.2.5. Reports -> Tabular -> "Print Custom Report" – click "Select Format"

12.4.3.2.5.1. On toolbar a "Select" icon will appear

12.4.3.2.5.2. Click on ManIntprepostRev.mac – click "Open"

Note: It is necessary to do this ***Every*** time a calibration is zeroed, even if the macro shows up in this field as the link to the macro that was lost when the calibration was zeroed.

12.4.3.2.6. Sample -> Default Sample

12.4.3.2.6.1. Change "Lab Prep Batch" field to the new Q-Batch #

12.4.3.2.6.2. Change "Client SDG" to be the instrument and date (i.e. 40MSV2-07252013)

12.4.3.2.7. Sample -> Surrogate/ISTD Parameter

12.4.3.2.7.1. Confirm that the correct IS/SS standard # is entered in the "Surrogate Lot#" field

12.4.3.2.7.2. Example - 51970:1.163 The 51970 is the IS/SS number followed by a colon followed by the volume added (this is a fixed amount unless change to the standard delivery has occurred.)

12.4.3.2.8. File -> Save Method

12.4.3.2.9. File -> Exit

12.4.3.3. **Process and Review Curve Data**

12.4.3.3.1. If significant Column maintenance was performed, it may be beneficial to process the 20 or 50 point first to update RT's as the larger concentrations will have better spectra to confirm correct identification

12.4.3.3.2. Select Method to calibrate and process files

12.4.3.3.2.1. Compound Sublist should be "all.sub"

12.4.3.3.2.2. Sample Type change to Calib Sample

12.4.3.3.2.3. Cal Level change to appropriate level 1-7

12.4.3.3.2.4. Double check that the Q-Batch # in MiscInfo and Lab Prep Batch are correct and match

12.4.3.3.2.5. Double check that the Client SDG reflects the instrument and date

12.4.3.3.3. Review Target Data

12.4.3.3.3.1. Review each analyte of all points for correct spectrum, RT and appropriate integration

12.4.3.3.3.2. All Manual Integration of all curve points and ICV need to have Review Codes added

12.4.3.3.3.3. After reviewing all points, review each analyte point 1 -> 7 to ensure consistent RT, spectra and Integration (i.e. shoulders cropped or included, etc.)

12.4.3.4. **Review Curve in Target Method**

12.4.3.4.1. Edit Method

12.4.3.4.2. Edit Compound -> Calibration

12.4.3.4.3. Review each analyte to ensure Initial Calibration % RSD are less than 15.0%

12.4.3.4.3.1. Note analytes > 15% and re-examine target data for proper integration

12.4.3.4.4. Check that all CCC compounds are less than 30% RSD

12.4.3.4.4.1. CCC's are 11DCE, chloroform, 12DiChloropropane, toluene, ethylbenzene and vinyl chloride

12.4.3.4.4.2. Instrument maintenance must be performed to correct problem if any >30%

12.4.3.4.4.3. If RSD >15% and <30% note %RSD to record later

12.4.3.4.5. Check that all minimum relative response factors (RRF) were met for the SPCC – Chloromethane, 11DCE, bromoform are 0.1 and 1122PCA, chlorobenzene are 0.3 – if any %RSD >15 not RRF to record later

12.4.3.4.6. If %RSD >15% - Drop Upper or lower point to achieve %RSD <15

12.4.3.4.6.1. If the Report Limit (RL) for analyte is not the 1 point, can the 1 point be disabled

12.4.3.4.6.2. Can the 7 point be dropped (or 6&7 points) - ** Will require lowering Max Amount

Note: ONLY upper or lower points can be dropped, ***Never*** an intermediate point!!

12.4.3.4.6.3. Must have minimum of 5 points for Averaged RF curve

12.4.3.4.6.4. After disabling appropriate points – Click "Update Calibration" button

12.4.3.4.7. Is %RSD still >15 – Switch Curve fit to Linear Regression
12.4.3.4.7.1. Change curve fit to Linear
12.4.3.4.7.2. **CCC Compounds (11DCE, chloroform, 12dichloropropane, toluene, ethylbenzene, vinyl chloride) MUST still be <30% RSD.
12.4.3.4.7.3. Initial Calibration R^2 must be 0.990 or greater
12.4.3.4.7.4. Must have minimum of 5 points for Linear regression curve
12.4.3.4.7.5. b intercept should be as close to zero as possible
12.4.3.4.7.5.1. i.e. by dropping the 300 point does the intercept go from 0.1980442 -> 0.0681234
12.4.3.4.7.5.2. This will give less false positive hits but require linear range to be lowered to 2000 µg/L
12.4.3.4.8. If R^2 is not >0.990
12.4.3.4.8.1. Change curve fit to Quadratic
12.4.3.4.8.2. ***Must have minimum of 6 points**
12.4.3.4.8.3. R^2 must be 0.990 or greater
12.4.3.4.8.4. Like Linear regression the 300 point can be dropped (or 1 point added if RL is 5 µg/L) to achieve the intercept closest to zero, as long as 6 points remain and linear range is adjusted.
12.4.3.4.9. If calibration for compound will not pass
12.4.3.4.9.1. The instrument cannot be run for lists including these analytes
12.4.3.4.9.2. Document analytes as failing in Run logbook
12.4.3.4.9.3. Place Post-It-Note on Instrument Terminal to alert other analysts of failures

12.4.3.5. **Update Linear Range**
12.4.3.5.1. After all analyte curve fits have been checked
12.4.3.5.1.1. Compound ->Edit Compound -> Report Parms
12.4.3.5.1.2. Adjust "Max Compound Amt Limits" to reflect highest point used (300->200 if 7th point was dropped)
12.4.3.5.2. Sublists -> Update Sublists
12.4.3.5.2.1. Check the "Update Sublists QC Limits" box
12.4.3.5.2.2. Highlight first sublist and hit Enter button
12.4.3.5.2.3. Arrow down to the next sublist and hit Enter
12.4.3.5.2.4. Repeat for all Sublists
12.4.3.5.2.5. **If you fail to update all the sublists, detects above linear range will not be "a" flagged in target.
12.4.3.5.2.5.1. EpicPro used the "a" flag to switch Condition Code from "OK" to "OR"

12.4.3.6. **Lock Method**
12.4.3.6.1. Security -> Initial Calibration Locked
12.4.3.6.2. Note: Do not select "Method Locked" – This would not allow the method to be used to process data

12.4.3.7. **Verify Initial Calibration**
12.4.3.7.1. View -> Initial Calibration
12.4.3.7.2. This generates a report with calibration data that will appear on the lower tool bar
12.4.3.7.3. Print report and review
12.4.3.7.3.1. The Calibration File Names in the header match the ***correct*** files used in the curve
12.4.3.7.3.2. All Average Response Factors < 15% and at least 5 points were included
12.4.3.7.3.3. All Linear Regression >0.990 and at least 5 points were included

12.4.3.7.3.4. All Quadratic > 0.990 and at least 6 points were included
12.4.3.7.3.5. Are all low points dropped below Report Limit for that analyte
12.4.3.7.3.6. Any high points dropped verify that the Max on Column was lowered and Record max amount on the report
12.4.3.7.3.7. No midpoints of curve are missing
12.4.3.7.3.8. All CCC compounds averaged – If not is the %RSD < 30% - Record actual RSD on report
12.4.3.7.3.9. All SPCC minimum RF factors met – If not averaged, switch to Averaged in method record the RF on the report and switch curve back to appropriate curve fit
12.4.3.7.4. Manually check individual Response Factors (RF) for at least one analyte
12.4.3.7.4.1. Calculation the RF for each point in the curve of an Averaged curve fit using the following formula
12.4.3.7.4.1.1. RF = (Area of analyte*concentration of IS) / (Area of IS * concentration of analyte)
12.4.3.7.5. Save method and Exit

12.4.3.8. **Re-quantify and Uploading Curve and ICV**
12.4.3.8.1. Select Method
12.4.3.8.2. Highlight Curve and re-quantitate
12.4.3.8.3. Process ICV – Must use all.sub (or Full.sub)
12.4.3.8.4. Review ICV and check CLP.rp
12.4.3.8.4.1. All SPCC Minimum RF must be met (if analyte is linear, must hand calculate)
12.4.3.8.4.2. All CCC Analytes must be <20%
12.4.3.8.4.3. All other analytes must be <30%
Note: Up to 5% (5 Analytes for a full list spike) may be between 30-40%)
12.4.3.8.4.4. All Analytes >40% will be flagged as failing
12.4.3.8.4.4.1. Document analytes as failing in Run logbook
12.4.3.8.4.4.2. Place Post-It-Note on Instrument Terminal to alert other analysts of failures
12.4.3.8.5. Generate all files to paperless (BFB, Curve and ICV)
12.4.3.8.6. Upload all files to EpicPro (double check Q-Batch is correct prior to upload)
12.4.3.8.7. Check Q-Batch in Epic to ensure Curve, BFB, and ICV imported correctly (may take several minutes)

12.4.3.9. **MN Low Standard Verification**
12.4.3.9.1. Copy 1ppb, 5ppb, & 20ppb files into another folder (i.e. the unprocessed blank following 300ppb)
12.4.3.9.2. Paste all 3 files than Rename (example 07251305.D -> MN01-07251305.D)
12.4.3.9.2.1. This will allow original files to be un-manipulated
12.4.3.9.3. Cut files and paste back in original folder
12.4.3.9.4. Re-Quant new MN files as LCS
12.4.3.9.4.1. Sample Type = QC Control Sample
12.4.3.9.4.2. Click QC Sample Type
12.4.3.9.4.2.1. Sample Type = LCS
12.4.3.9.4.2.2. Spike List = MNLOW1.spk, MNLOW5.spk, MNLOW20.spk
12.4.3.9.5. Highlight all 3 files and Do Quick Forms – Form 3 of LCS

12.4.3.9.6. Print Form 3.s and pass on to Supervisor to update MN report limits in EpicPro

12.4.3.10. **Before proceeding with analysis of samples**

12.4.3.10.1. Check Chemstation sequence that correct Q-Batch is in BFB and CCC

12.4.3.10.2. Check that correct Method is referenced in the sequence

12.5. Sample Preparation

12.5.1. Samples

12.5.1.1. **Sample Pre-screening**

12.5.1.1.1. Samples are pre-screened using a rapid GC headspace technique. See SOP S-GB-O-001 *Sample Screening Volatile Organics Prior to Preparation* (most current revision or replacement**)** for the specifics on the pre-screening of samples.

12.5.1.2. **Water Samples**

After pre-screening, water samples typically do not require any sample preparation unless they require a dilution to bring high-level contaminants within calibration range or to minimize matrix interference. Dilutions are made following Section 12.5.1.5.1.

After analysis check the residue in the vial following analysis using pH paper. The pH should be <2. Document results in the run sequence log as <2 or >2. Footnote any sample not meeting the pH requirement. If dilutions are required, pH preservation can be verified at the time the dilution is made using the sample remaining in the original sample container.

12.5.1.3. **Soil Samples**

12.5.1.3.1. **Low concentration soils**

Samples received for low level analysis should be contained in pre-weighed VOA vials either with or without Reverse Osmosis Water (ROW) and/or sodium bisulfate preservative. NOTE: some samples may be received in coring devices (e.g. Encore™, etc.). These samples must be extruded into a VOA vial either with or without ROW and/or sodium bisulfate and a magnetic stir bar within 48 hours of sample collection. If samples are received that are greater than 10g the PM must be notified and samples will be rejected for analysis.

12.5.1.3.1.1. **Weight determination:** Prior to preparation or analysis of any soil received in a pre-weighed VOA vial, the sample weight must be determined and recorded. Accurately weigh the VOA vial to 0.01 g in the laboratory; record this amount in the sample preparation logbook. Subtract the tare weight recorded on the vial and 0.18g for each Pace Sample label that was affixed to the pre-tared vial; this will be the weight of sample in the vial.

12.5.1.3.1.2. Samples received pre-weighed in the field must be in 40 mL VOA vials and contain a magnetic stir bar, acid preservative and a

field tare weight. The analyst will compare the field tare weight to the weight of the sample before analysis. The weight of the sample should be recorded.

12.5.1.3.1.3. All samples must be extruded from the coring devices within 48 hrs. of collection. If the samples are to also be analyzed within the 48 hr criteria, no acid preservation is required. If analysis is to occur after 48 hrs. but within 14 days, the samples must be preserved with Sodium Bisulfate or if preserved with ROW, stored frozen. The ratio of Sodium Bisulfate to sample weight is 0.2g of preservative to 1g of sample.

12.5.1.3.2. **High concentration soils**

12.5.1.3.2.1. **Methanol-Preserved Samples:** Samples received in pre-weighed vials preserved with methanol must be accurately weighed in the laboratory to 0.01 g and the sample weight determined. See Section 12.5.1.4.2.1.2. Subtract the tare weight written on the VOA vial and 0.18g for each Pace Sample label that was affixed to the pre-tared vial from the weight determined in the laboratory. This will be the weight of sample in the VOA vial. The volume of methanol in the sample container should be at a 1 to 1 ratio of soil to methanol.

12.5.1.3.2.1.1. **Calculation of 1:1 ratio soil (g) to MeOH (mL).**

To calculate the amount of soil weight (g) in the sample can be calculated as follows:

Where:

$W_S = W_T - W_J - (N * W_l)$

W_s = Weight of soil in the sample (g)
W_t = Total weight of the sample including vial, cap, soil, and MeOH (g)
W_J = Weight of the jar including the vial, cap, and MeOH (g)
N = Number of Pace Sample labels
W_l = Weight of Pace Sample label affixed to the pre-tared 40mL VOA vial; which has been determined to be 0.18g

To calculate volume of MeOH to achieve the 1:1 ratio of soil weight (g) to MeOH (mL) may be calculated as follows:

Where:

$V_M = W_S - 10mL$

V_M = Volume of MeOH required to achieve 1:1 ratio of soil (g):MeOH (mL)
W_S = Weight of soil in the sample (g)
10 = Volume of MeOH initially added (mL)

12.5.1.3.2.2. **Unpreserved Samples**: Samples received in unpreserved pre-weighed vials must be accurately weighed in the laboratory to 0.01 g. NOTE: some samples may be collected and transported to the laboratory in bulk containers. An accurately weighed ≥5 gram sub-sample must be taken and added to a 40mL VOA vial. The non-compliant sample collection technique must be recorded in the preparation logbook and a qualifier added to the sample result. The samples are then preserved with 10 mL methanol within 48 hours of sample collection. To determine the sample weight: subtract the weight written on the VOA vial from the weight determined in the laboratory prior to the addition of the 10 mL methanol preservative. This will be the weight of sample in the VOA vial.

12.5.1.3.2.3. The balance is to be leveled before calibration. Calibration verification of the analytical balance is done with S-class weights. These values are to be noted in the Balance calibration logbook. The frequency of balance calibration verification is once per day before the balance is used or when the balance is moved.

12.5.1.4. **Dilutions**

12.5.1.4.1. **Water**

Dilutions on aqueous samples must be prepared in a volumetric fashion. Sample aliquots may be measured in either a volumetric pipette or syringe and brought to volume in a volumetric flask.

12.5.1.4.1.1. All steps must be performed without delays until the diluted sample is in a 40 mL VOA Vial.

12.5.1.4.1.2. Dilutions are made in gastight 50mL syringes.

12.5.1.4.1.3. Calculate the approximate volume of organic-free reverse osmosis water (ROW) added to the syringe and add slightly less than this quantity of ROW to the syringe barrel.

12.5.1.4.1.4. Inject the proper aliquot of sample using the appropriate 10µL to 5mL syringes to create the desired dilution in the 50 mL syringe. Dilute the sample to the mark with ROW. Invert, and rock back and forth three times. Repeat the above procedure for additional dilutions.

12.5.1.4.1.5. Fill a 40mL VOA vial with the diluted sample from the 50 mL syringe prepared in Section 12.5.1.5.1.4.

12.5.1.4.1.6. Place the VOA vial on the autosampler. All dilutions should keep the response of a major constituent (previously saturated peaks) in the upper half of the linear range of the curve.

12.5.1.4.1.7. The autosampler will add the internal standard and surrogate to the sample and transfer 5 mL over to the 5 mL sparge tube on the concentrator.

12.5.1.4.2. **Soil**

12.5.1.4.2.1. **Low Level Soils**

12.5.1.4.2.1.1. It will be necessary to adjust the sample weight for

quantitation purposes. Any analyte hits outside of the calibration range, 200 µg/kg, will be extracted into Methanol and analyzed under High Concentration Sample criteria.

12.5.1.4.2.2. **High Concentration Soils**

12.5.1.4.2.2.1. Dilute all samples according to the results of the screening data. A standard analytical dilution is 1:50. Add 1.0 mL of the sample extract measured with a microsyringe of appropriate volume to 49 mL of reverse osmosis water in a 50 mL syringe.

12.5.1.4.2.2.2. To make dilutions other than a standard 1:50 dilution, fill a 50 mL syringe to a volume of 49 mL with reverse osmosis water. Using a 1.0 mL syringe, inject methanol into the 50 mL syringe to bring the total volume of sample and methanol to equal 1.0 mL. Using an appropriate volume syringe, inject the sufficient amount of sample to reach desired dilution. Invert, and rock back and forth three times.

12.5.1.4.2.2.3. The 50 mL syringe contents are place into a 40 mL VOC vial by slowly deploying the plunger and injecting on the side of the vial to eliminate cavitation and loss of analytes to volatilization or sparging. Enough of the contents are injected to created a meniscus at the top of the vial that when capped will produce a no headspace sample.

12.5.1.4.2.2.4. The vial is capped and checked for headspace. If vial is free of headspace, it is ready for analysis as per Section 14.

12.5.2. Batch QC

Refer to Table 13.1 for details on Batch QC requirements.

12.5.2.1. **Method Blank**

12.5.2.1.1. **Water**

12.5.2.1.1.1. Fill a 40mL VOA vial with reverse osmosis water (ROW) and place in autosampler rack. The autosampler will add the internal standard and surrogate to the sample and transfer 5mL over to the 5mL sparge tube on the concentrator.

12.5.2.1.1.2. When leach samples are present, one leach blank must be analyzed with the analytical batch in addition to the method blank.

12.5.2.1.2. **Low Level Soil**

12.5.2.1.2.1. A method blank is prepared with 5 mL of ROW into a 40 mL VOA vial containing a disposable magnetic stir bar. The vial is placed onto the autosampler and the autosampler will add the internal standard and surrogate to the sample. The blank is preheated to 40°C and purged. The method blank must be analyzed under the same criteria as the samples.

12.5.2.1.3. **High Concentration Soil**

12.5.2.1.3.1. The method blank (extraction blank) is made by adding 10 µL of

the 2500 ppm surrogate standard in 10 mL methanol placed in a 40 mL VOA vial containing 10g of Ottawa sand. A 1.0 mL portion of this is diluted with 49 mL of ROW for a final concentration on the instrument of 50 µg/L.

12.5.2.2. **Laboratory Control Sample/Laboratory Control Sample Duplicate**

12.5.2.2.1. See Table 10.7 for spiking procedures and Table 13.1 for Batch Quality Control Criteria.

12.5.2.2.2. A Laboratory Control Sample Duplicate is required when sample volume for the Matrix Spike/Matrix Spike Duplicate is not received.

12.5.2.2.3. When EPA 624 samples are present with SW846 8260B samples, one LCS/D at 20 µg/L and one LCS/D at 50 µg/L must be analyzed to meet each method requirement. If the 20µg/L LCS/D is valid, the additional 50 µg/L LCS/D pair is not required.

12.5.2.3. **MS/MSD Samples**

12.5.2.3.1. See Table 10.7 for spiking procedures and Table 13.1 for Batch Quality Control Criteria..

12.5.2.3.2. When one to 20 EPA 624 samples are present one MS/MSD pair should be analyzed for every 20 samples (or one spiked sample per month) at a concentration of 20µg/L.

12.5.2.3.3. When Leach samples are analyzed, one MS must be analyzed per each sample matrix submitted for leaching.

13. Quality Control

13.1. Instrument Quality Control: Refer to Table 11.2 for initial and continuing calibration criteria and corrective actions.

13.2. Batch Quality Control

Table 13.1 – Batch Quality Control Criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reverse Osmosis water (ROW)	One (1) per 20 samples or 12 hour window (whichever is most frequent)	Target analytes must be less than reporting limit. If results are reported to MDL, target analytes in MB should be non-detect	Re-analyze associated samples. ***Exceptions:*** 1. If sample ND, report sample without qualification 2. If sample result >20x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination. 3. If sample result <20x MB detects, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	Method specified compounds: Benzene, Chlorobenzene, 1,1-Dichloroethene, Toluene, Trichloroethene *OR (alternative)* Full Target List compounds	One (1) per batch of up to 20 samples	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to NELAC 2003 Chap 5 D.1.1.2.1.e	Analyze a new LCS If problem persists, check spike solution Perform system maintenance prior to new LCS run ***Exceptions:*** 1) If LCS rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. Note: The State of South Carolina does not allow the use of Marginal Exceedances.
Laboratory Control Sample Duplicate (LCSD)	Method specified compounds: Benzene, Chlorobenzene, 1,1-Dichloroethene, Toluene, Trichloroethene *OR (alternative)* Full Target List compounds	One (1) per batch of up to 20 samples	Laboratory derived limits Method Specified List: All compounds must pass control criteria, with no exceptions. Full Target List: Marginal exceedances allowed according to NELAC 2003 Chap 5 D.1.1.2.1.e	Analyze a new LCSD If problem persists, check spike solution Perform system maintenance prior to new LCSD run ***Exceptions:*** 1) If LCSD rec > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. Note: The State of South Carolina does not allow the use of Marginal Exceedances.
Matrix Spike (MS)	Method specified compounds: Benzene, Chlorobenzene, 1,1-Dichloroethene, Toluene, Trichloroethene *OR (alternative)* Full Target List compounds	One (1) per batch of up to 20 samples, must include one TCLP MS for any analyzed in sequence	Laboratory derived limits	If LCS/LCSD and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One (1) for every 5% of all environmental samples	Laboratory Derived Limits	Report results with an appropriate footnote.

13.3. Sample Quality Control

Table 13.2 – Sample Quality Control criteria

QA Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	Pentafluorobenzene 1,4 Difluororobenzene 1,4-Dichlorobenzene-d4 Chlorobenzene-d5	Added to all standards, samples, spikes, control samples, and method blanks prior to analysis	**Retention Time:** RT must be ± 30 seconds from last calibration check on all samples	**Retention Time Failure:** 1. If matrix interference is NOT probable, the analytical system must be checked for source of retention time shifting. 2. Affected samples should be reanalyzed in the absence of an obvious instrument or matrix related interference.
Surrogate Standards	Dibromofluoromethane Toluene-d8 4-Bromofluorobenzene	Added to all samples, spikes, control samples and method blanks prior to analysis	Laboratory derived limits	1. Check system parameters 2. Identify and correct likely cause 3. Re-run samples ***Exceptions:*** 1. Surr rec above criteria and target compounds < RL, result may be reported with appropriate footnote. 2. Surr rec out of control due to obvious sample matrix interference (i.e. co-elution), report results with appropriate footnote.

14. Data Analysis and Calculations

14.1. Analyze Samples

14.1.1. Water Samples

14.1.1.1. Create run sequence log. Place 40 mL VOA vial containing sample (Section 12.5.1.2), or appropriately diluted 40 mL VOA vial containing sample (Section 12.5.1.5.1) onto the autosampler. The autosampler will add the internal standard and surrogate to the sample and transfer 5 mL over to the 5 mL sparge tube on the concentrator.

14.1.2. Low-level Samples

14.1.2.1. Create run sequence log. Place the already weighed 40 mL VOA vial containing the sample, stir bar and 5 mL of reverse osmosis water (ROW) or Sodium Bisulfate solution (Section 12.5.1.4.1) onto the autosampler where another 5 mL of ROW and internal standard and surrogate will be added by the autosampler. The sample is preheated to 40°C and purged. The stir bar is moving continuously during the purge cycle. This also helps in compound recovery by breaking down any clumps that may remain in the sample.

It will be necessary to adjust the sample weight for quantitation purposes. Any analyte hits outside of the calibration range, 200 µg/kg, will be extracted into Methanol and analyzed under High Concentration Sample criteria.

14.1.3. High Concentration Samples

14.1.3.1. Create run sequence log. Place 40 mL VOA vial containing sample (Section 12.5.1.4.2), or appropriately diluted 40 mL VOA vial containing sample (Section 12.5.1.5.2.2) onto the autosampler. The autosampler will add the internal standard to the sample and transfer 5 mL over to the 5 mL sparge tube on the concentrator

14.2. Data Reduction

14.2.1. Qualitative Analysis

Retention Time Comparison: The relative retention time (RRT) of the sample component must be within ±0.06 RRT units of the component in the calibration verification standard. Extracted Ion Current Plots (EICPs) may be used to provide a more reliable assignment of RT in the presence of co eluting components.

Mass Spectrum Comparison: The characteristic ions from the reference mass spectrum are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

- The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other.
- The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.
- Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times.
- Compare computer-matched compounds with reference spectra to accept or reject each identification.
- All ions present in the reference spectrum that are at least 10% of the base peak must be present in the sample background-subtracted spectrum.
- The relative intensities of these ions must agree within ± 30% between the standard and sample spectra.
- While this is a good guideline, acceptance or rejection will depend upon the judgment of the analyst\

Carry-Over Protocol: Each sample must be closely evaluated to confirm that reported values are not a result of carry-over from a previous sample or QC standard. The blank(s) following the CCV or batch QC can be evaluated to determine typical amounts of carry-over to be expected from a sample with results around the mi-range of the curve (i.e. naphthalene and hexachlorobutadiene may carry over 0.5-2ppb from a 50ppb detect whereas vinyl chloride or ketones generally do not have any carry-over at the same concentration). Additionally, the blank(s) following the upper point of an ICAL can demonstrate carry-over of compounds at the upper end of the curve. Obviously, carry-over results vary from instrument to instrument and even ICAL to ICAL; therefore, when there is any question of carry over, an example of similar hits on that particular instrument's recent analysis are to be considered (i.e. a sample earlier in the sequence had benzene hit of 200ppb and the following sample was ND; therefore, it would be reasonable to assume

that a benzene detect of 1.5ppb following a sample containing 100ppb of benzene was not a result of carry-over). Every possible attempt to avoid carry-over contamination in clients' samples will be taken. This may include running instrument clean up blanks following standards that are known to carry-over or following samples that are known to have high concentrations of contaminants, or attempting to run groups of similarly concentrated samples together instead of intermittently through a sequence. When highly contaminated samples are grouped together it is to be expected that a percentage of a reported value may result from carry-over, in this case the significance of carry-over compared to reported value must be considered (i.e. a hit of PCE typically may carry-over 0.5ppb from a sample with an on-column concentration of 100ppb; therefore, a sample with concentration of 70ppb following a sample with a concentration 100ppb may contain roughly 0.5ppb of PCE resulting from carry-over which should be deemed insignificant). Similar to rules concerning Method Blank contamination, if the reported result is greater than 20 times the expected carry-over concentration, the resulting carry-over should be considered insignificant and value acceptable to report.

14.3. Quantitative Analysis – Quantitation is based on the integrated abundance of the target analyte's quantitation ion using the internal standard technique.

Raw Data Results: The GC/MS data system will calculate the concentration of each analyte as µg/L (or ng/mL). For water samples, no further calculations are necessary unless a dilution of the sample has been performed. If the initial analysis of the sample or a dilution of the sample has a concentration that exceeds the calibration range, the sample must be analyzed at a higher dilution. All dilutions should keep the response of the major constituents in the upper half of the linear range of the curve.

14.4. Calculation – Aqueous Sample:

$$\text{Concentration } (\mu g/L) = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

Where:

A_x= Area of characteristic ion for compound being measured.
I_s = Amount of internal standard injected (ng).
A_{is} = Area of characteristic ion for the internal standard.
RF = Average Relative Response factor for compound being measured.
V_o = Volume of water purged (mL), taking into consideration any dilutions made.

14.5. Soil/ Solid calculations:

$$\textit{High}\ \text{Conc. (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

$$\textit{Low}\ \text{Conc. (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

Where:

A_x, I_s, A_{is}, RF = Same as in water and water-miscible waste above.
V_t = Volume of total extract (mL).
V_i = Volume of extract added (mL) for purging.
S_v = Volume of diluted extract.
W_s= Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

14.6. Tentatively Identified Compounds (TICs) – For some samples, identification may be desired for non-target compounds. A mass spectral library search may be conducted to attempt assignment of tentative identifications. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications.

- Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See table in Section 13.

16. Corrective Actions for Out-of-Control Data

16.1. See table in Section 13.

17. Contingencies for Handling Out-of-Control or Unacceptable Data

17.1. If not specifically listed in the table in Section 13, the contingencies are as follows. If there is no additional volume to perform analyses, all data will be reported as final with applicable qualifiers.

18. Method Performance

18.1. Method Detection Limit (MDL) Study: An MDL study must be conducted annually per S-GB-Q-020, *Determination of the LOD and LOQ* (most current revision or replacement) for each matrix per instrument.

18.2. Demonstration of Capability (DOC): Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, *Orientation and Training Procedures* (most current revision or replacement).

18.2.1. Analysis of four (4) LCS for each matrix the analyst will be performing. The concentration for low level soil and methanol soils should be at the current LCS spike concentration and the recovery is to be within the current LCS QC limits. The concentration for aqueous DOC should be at 20 µg/L and the recovery is to be within the current LCS QC limits.

19. Method Modifications

Method modifications for EPA method 8260B and EPA 624 are as follows:

- Modifications should be targeted to improve quality, efficiency or the cost effectiveness of the procedure.
- All major modifications to the procedure that may directly affect data quality must be thoroughly documented. A new demonstration of capability and equivalency must be performed and kept on record.
- Procedures identified as “Best Practices” by the PACE 3P Program will be incorporated into this document as minimum requirements for Pace laboratories.
- If a client fails to provide the method required Matrix Spike/Matrix Spike Duplicate (MS/MSD), the laboratory will analyze a Laboratory Control Spike Duplicate to demonstrate precision. The analytical batch will be qualified with the “M5” data qualifier.

Method modifications for EPA method 5035 is as follows:

- The laboratory uses a modification of SW-846 Method 5035 for medium-level volatiles in soil. The laboratory uses 10 grams of soil and 10 mL of methanol whereas the method indicates 5 grams of soil and 5 mL of methanol.

- *Note*: Samples reported to the State of South Carolina requires the use of 5 grams of soil and 5 mL of methanol.

20. Instrument/Equipment Maintenance

20.1. See current version of SOP: S-GB-Q-008 *Preventative, Routine, and Non-routine Maintenance.*

21. Troubleshooting

21.1. See most current version of the Instrument Operations Manual.

22. Safety

22.1. Standards and Reagents: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Safety Data Sheets (SDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. Samples: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

22.3. Equipment: Portions of the analytical instrumentation operate at high temperatures and under positive pressure. Care must be taken to minimize accidents and injuries when working on or with this equipment. Instruments should be turned off or the heated zone temperatures lowered to reduce the risk of thermal burns. Allow adequate time for the equipment to cool prior to working on these specific zones.

The purge and trap concentrator and autosampler use gas under pressure to purge samples and, in some cases, drive the robotic assemblies. These high pressures introduce the risk of injury due to flying glass and other objects should a vessel or line rupture. Safety glasses are highly recommended at all times when working in, on or around these pieces of equipment. Even instrumentation that is not operating may contain portions of the system under pressure.

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-GB-W-001, *Waste Handling and Management* (most current revision or replacement).

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (i.e. before a reagent expires)

24. Pollution Prevention

24.1. The company wide Chemical Hygiene and Safety Manual contains additional information on pollution prevention.

25. References

25.1. Pace Quality Assurance Manual- most current version.

25.2. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.3. USEPA, SW-846, Method 8260B, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), December 1996.

25.4. USEPA, SW-846, Method 5030B, "Purge and Trap for Aqueous Samples," December 1996.

25.5. USEPA, SW-846, Method 5035A, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," Draft Revision 1 July 2002.

25.6. USEPA, SW-846, Method 8000B, "Determinative Chromatographic Separations", December 1996.

26. Tables, Diagrams, Flowcharts, Attachments, Appendices, etc.

26.1. Attachment I: Flow Chart

26.2. Attachment II: Client Specific Requirement Statement

26.3. Attachment III: Master Guide to Passing BFB for Agilent MSD Modes 5970-5973

26.4. Attachment IV: Agilent Document: BFB Tuning for Environmental Analysis: Three Ways to Succeed.

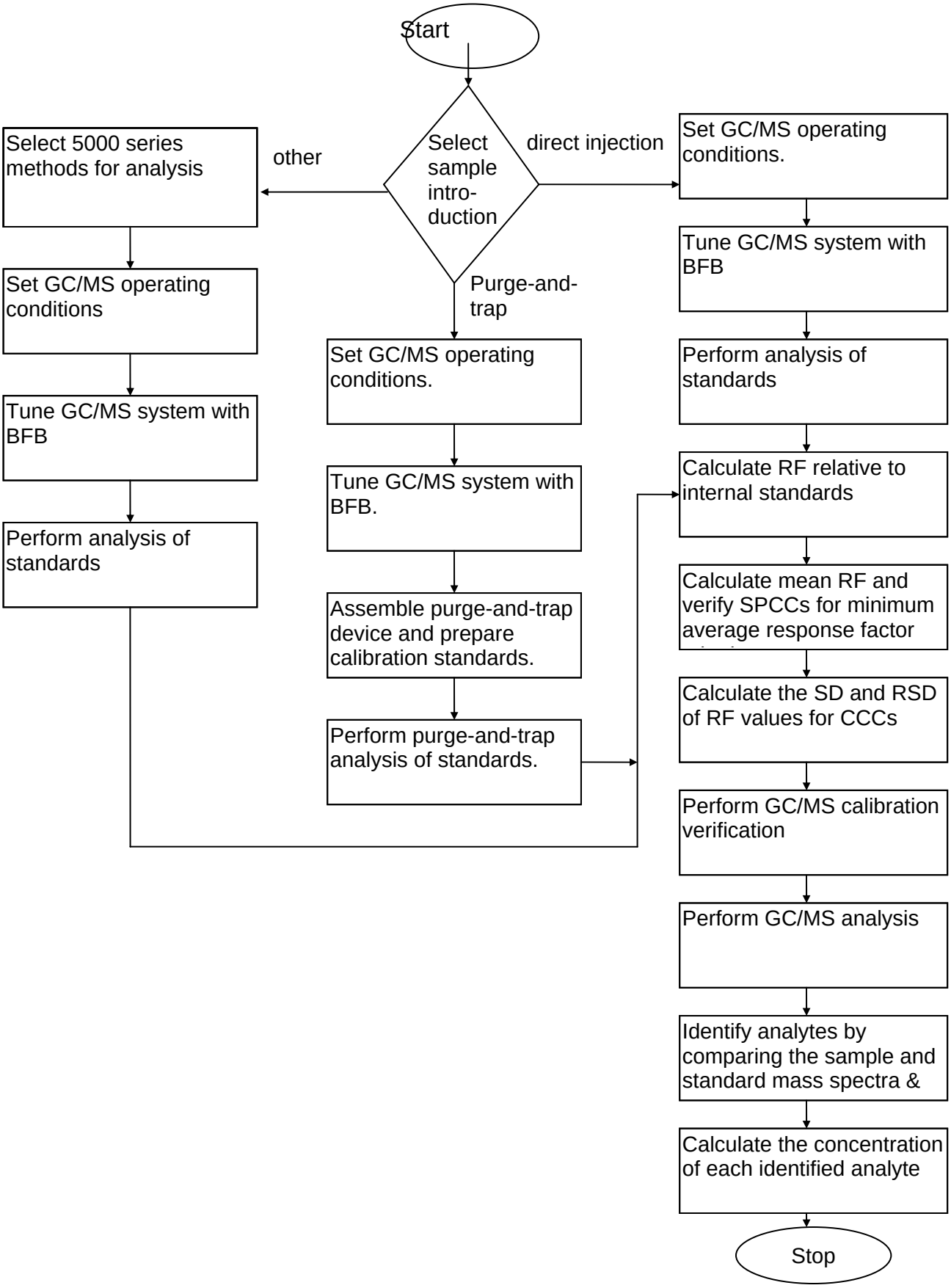
26.5. Attachment V: VOA Calibration Process

26.6. Attachment VI: VOA Calibration Checklist

27. Revisions

Document Number	Reason for Change	Date
S-GB-O-056-Rev.08	Section 2, 10.1: Added information for Nitrogen purge. Table 7.1: Updated samples to 3 vials. Table 9.1: Updated Serial Number for equipment, added 40MSVC. Tables 10.3, 10.4, 10.6, and 10.7: Updated standard information. Table 11.1: Added 1-Methylnaphthalene Section 12.4: Added Operation of the Software Systems Section 12.5.1.4: Incorporated label weight of 0.18g into determinations. Attachments V and VI: Added.	09May2014
S-GB-O-056-Rev.09	Table 7.1: Updated preservation requirement to ≤6°C from 2±4°C to match 40CFR. Table(s) 10.6, 10.7, and 11.1: Added information for CAL-3 on the water curve. Table 10.7: Added CAL 7 Curve information. Table 13.1: Added ME requirements for SC requirements. Section 25: Added Pace QM and TNI references.	02Dec2014
S-GB-O-056-Rev.10	Table 9.1: Removed 40MSV9 from instrument list; removed serial numbers from SOP. Table 10.3: Updated Stock Standards. Table 10.4: Added compounds to O2Si custom mix (changed from Restek); Removed Restek custom mix; Added compounds to 4.1 Mega Mix.	19Aug2015
S-GB-O-056-Rev.11	Throughout Document: Updated Pace Analytical Services, Inc to Pace Analytical Services, LLC Section 14.2: Added Carry-over protocols.	21Jun2017

FLOWCHART


Start
Select sample intro-duction
other
direct injection
Purge-and-trap
Select 5000 series methods for analysis
Set GC/MS operating conditions
Tune GC/MS system with BFB
Perform analysis of standards
Set GC/MS operating conditions.
Tune GC/MS system with BFB.
Assemble purge-and-trap device and prepare calibration standards.
Perform purge-and-trap analysis of standards.
Set GC/MS operating conditions.
Tune GC/MS system with BFB
Perform analysis of standards
Calculate RF relative to internal standards
Calculate mean RF and verify SPCCs for minimum average response factor
Calculate the SD and RSD of RF values for CCCs
Perform GC/MS calibration verification
Perform GC/MS analysis
Identify analytes by comparing the sample and standard mass spectra &
Calculate the concentration of each identified analyte
Stop

Attachment II:

Throughout document, reference to Client Specific requirements refers to samples analyzed following the BP Technical Requirements LaMP Revision 10.1, Canadian National Railway Services and Technical Specifications Manual.

Attachment III: Master Guide to Passing BFB for Agilent MSD Modes 5970-5973.

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Master Guide to Passing BFB for Agilent MSD models 5970-5973

The Importance of Thermal Stabilization

Before we begin discussing tuning let me make an important point. If a GC/MS has been vented, it takes quite a while for the system to thermally stabilize. So, even if you reached your ultimate pressure and all heated zones are at their setpoint and the high vacuum pump is at its setpoint, don't be fooled into thinking the mass spec has thermally stabilized. Even though the temperatures are at their setpoints, it takes several hours for the heat to fully disseminate throughout the analyzer. You can certainly run the systems prior to thermal stabilization, but don't be surprised if the system changes while you do it. Use the following guide as to how long thermal stabilization should take:

Model MSD	Typical time for thermal stabilization
5970	16 hours
5971	8 hours
5972	8 hours
5973	8 hours

Creating and Maintaining an Optimized Manual Tune File for BFB

OK, so let's assume your system has reached thermal stabilization and has passed Autotune. You now want to manually tune the system for BFB. Here is the procedure I use to take an Autotune file and generate a Manual Tune File for the MSD systems for both 524.2 and 624/8260:

Set the Oven Temperature to the temperature at which BFB elutes in your program. Since sensitivity is flow dependent, and flow is temperature dependent, we want to tune the system under the *same* conditions that BFB will experience when it elutes. Generally this temperature is around 150°C, depending on your configuration.

Change the scan range from 10-800 or 10-600 AMUs (or whatever it is in AUTOTUNE) to 10-300 AMUs. Most EPA Methods for Volatiles specify a 35-300 AMU range so 10-300 is fine.

We want to scan in the 10-29 range so we can leak check as we tune. We don't want to scan above 300 amus when we tune for BFB because that's not what the method stipulates. Set the 3 ions that are monitored from 69-219-502 to 69-131-219.

Once you have verified that no leak exists (the kind of leak where air gets sucked into the system), you can set the scan range to 35-300 (or whatever you use in your acquisition method). This isn't necessary but some analysts find it helpful. If you do this, be sure to reset the scan range to 10-300 each time you retune to check for air leaks and if none exists set it back to 35-300 amu.

At this point you need to establish in your mind the target relative abundances of 131 and 219. A good starting point would be 35-40% of each relative to ion 69.

Set the X-ray lens to maximize on ion 131 (5970, 5971, 5972). Theoretically ion 3 ions should maximize at the same point but sometimes the ramp is a bit skewed.

Our next step is to lower 219 (which should be around 60% or so from Autotune) and bring it even with 131 and to about 35-40% of ion 69 . Generally, 131 is about 20% lower than 219 in Autotune. Both of these can be achieved by doing the following:

raising the Ion Focus from at or near 0 (where it should be after Autotune) to about 30-80 Volts for 5970

raising the Entrance Lens Offset from below 8 (where it should be after Autotune) to about 15-20 for 5971, 5972, 5973.

Since raising the Ion Focus/Ent Lens Offset increases overall sensitivity, after step 4 is done we will need to *lower* the EM voltage to stay on scale. Generally, aim for between 2-4 million counts of Ion 69 adjust the EM in to keep the same abundance throughout the tuning procedure.

Do Peak width and Mass Axis calibrations. At this point, you can use the automated feature whereby the software does it for you. Later on, we can tweak it using the AMU Gain and AMU Offset if necessary.

Make minor adjustments in the Entrance Lens (5970) and Entrance Lens and/or Ion Focus (5971,2,3) to fine tune your ratios. Additionally, you can make minor adjustments on the Repeller if needed to fine tune ratios, but only do this as a last resort.

Try to keep the Repeller setting <u>constant</u> and set to whatever it sets it to in AUTOTUNE.

Often you need to go back and forth between both lenses to zero in on your target ratios. Remember to adjust the EM voltage to maintain proper abundance of ion 69.

Do Peak width and Mass Axis calibrations. Your masses obtained in Spectrum Scan (*not* Profile Scan which tells you Peak Width, not Mass Axis) should be the integer +-0.1 AMUs (i.e. 68.90-69.10 etc.). If this cannot be obtained automatically by the software, a hardware problem may exist.

Peak widths for all three ions should be between 0.47-0.54 AMUs, as close to 0.50 AMUs as possible (although in my experience 0.52 seems to be a little better). If they are not, they can be narrowed by increasing the AMU Gain and AMU offset and widened by decreasing either or both of these settings. If you cannot achieve ratios between 0.47-0.54 AMUs for all three ions, a hardware problem may exist.

For the 5971, 72 and 73s, you can also fine tune the width of ion 219 with the "219Wid" setting, although keep in mind that adjusting that also affects the 131 peak width as well.

Save the settings under a new name (or overwrite BFB.U if that file already exists) and run your BFB. It will usually pass. If not, the system must be re-tuned. Some systems require ion 131 to be greater than 219 (typically 40-35 or 35-30 , etc.); others require ion 219 to be greater than 131 (typically 40-35 or 35-30 , etc.). Adjustment of these ratios can be achieved by varying the Ion Focus and/or Entrance Lens Settings (especially the Entrance Lens). If you cannot pass BFB by having 131=219, or 131<219 by about 5-15%, or 131>219 by about 5-15%, this indicates that a problem exists. You should not have to obtain any weird abundances to make BFB pass. Generally, a system with 131 and 219 about the same abundance and both between 25-45% of 69 will pass. But since each system is unique and all will change with time and usage you must get a feel for what works best for your system.

Remember: once you have a good Tune File, you should check the tune each day and make whatever adjustments are necessary to keep ratios, abundances, and peak widths constant; this is fundamentally important in maintaining linearity and consistency in your analytical runs. You don't need to re-run Autotune each day- go directly to Manual Tune and adjust the system to look as it did the day before. Do this each day and you will be doing quite a bit to help your system stay linear.

So now we run our BFB and it will usually pass at the apex. But what if it doesn't? What if our relative ratios and peak widths of ions 69-131-219 are exactly what we think they should be and exactly what's been working for the last few months? What do we do then? We'll review the acceptance criteria for BFB (and since various methods have various criteria we will use the tightest acceptance criteria), what can fail, and how to modify your tune file to make BFB pass.

Remember: GC/MS systems are dynamic instruments: their sensitivities and responses change with time and usage, and what works today on your system may not work forever; it's essential that good GC/MS analysts understand tuning and be able to fine-tune (no pun intended) you systems to pass BFB and keep it running optimally.

Let's begin by assuming we have tuned our instrument to have all peak widths at or near 0.50+-0.05 amus, the mass axis of ions 69,131 and 219 are all +-0.1 amu, and the relative rations of 69-131-219 are 100%-35%-35% respectively. We run our BFB and it fails. We then MUST make adjustments to our Manual Tune file based on what failed, correct our ratios and/or peak widths accordingly, and rerun BFB.

I will give some guidelines to follow in modifying your tune file. If these guidelines fail to make BFB pass, a hardware problem may exist.

The chart below lists the acceptance criteria for BFB we will use in this discussion. Keep in mind that some methods and stage agencies allow you to use the Apex, The Apex + 1 scan, The Apex + 1 scan or a 3-scan average of them so be sure you're trying all the legal scans in the peak. Using scans other than the Apex and one scan to either side should not be used. Also, if you have a significant baseline you should obtain a background subtracted mass spectrum.

Acceptance criteria for 4-Bromofluorobenzene for 624/8240

Source: EPA Method 624 for 50 ng injection

Mass	Acceptance Criteria	Affected by in Tune File
50	15-40% of mass 95	ratio of 69 to 131 and 219
75	30-60% of mass 95	ratio of 69 to 131 and 219
95	Base peak, 100% relative abundance	ratio of 131 to 69 and 219
96	5-9% of mass 95	peak width of ion 131
173	<2% of mass 174	peak shape of ion 219
174	50-99.9 of mass 95	ratio of 219 to 131 and 69
175	5-9 of mass 174	peak width of ion 219
176	95-101% of mass 174	ratio of 219 to 131 and 69
177	5-9% of mass 176	peak width of ion 219

As the chart illustrates, for every criteria of BFB there is a corresponding ion in the compound PFTBA (Perflourotributylamine) which is used during tuning. So if the BFB fails for one or more criteria, we adjust the ratios and/or peak widths of the PFTBA during tuning.

If you are having problems with BFB, ALWAYS check your high vacuum pressure. The discussion that follows assumes that your ion source pressure is consistent with what it historically has been. If not, that needs to be resolved first and foremost before any of the techniques presented here can be utilized.

We will now discuss each ion and what to modify in the Manual Tune file should it fail:

Ion 50 (Acceptance criteria: 15-40% of mass 95); Affected mainly by the ratio of 69 to 131 and 219 in our tune file. Tests for adequate low-end sensitivity.

Tuning issues that cause problems with this ion:

Generally, if ion 50 fails it is because it falls under the 15% minimum percentage criterion. Occasionally it will fail because it is >40% of mass 95. I have seen many instances where ion 50 ends up below 15% of mass 95. This means that the system is not sensitive enough at the low end. To remedy this, lower the relative ratios of 131 and 219 each by about 5%. This reduction of the mid-range ends up making the low end more sensitive and will boost the amount of ion 50 that is generated. If this fails, continue to lower the relative ratios of 131 and 219. If you need to make ions 131 and 219 below 20% of ion 69 for BFB to pass I would suspect a hardware problem might exist.

If ion 75 ends up being too high (greater than 40% of ion 95), you should try raising both ions 131 and 219. This increase in the mid-range ends up making the low end less sensitive and should reduce the amount of ion 50 that is generated. If this fails, continue to raise the relative ratios of 131 and 219. If you need to make ions 131 and 219 above 50% of ion 69 for BFB to pass I would suspect a hardware problem might exist.

Hardware issues that cause problems with this ion:

The most common hardware issues that cause failure of ion 50 would be a dirty source (especially if you have elevated amounts of ion 50 AND elevated amounts of ion 75), problems with the rough pump (also for elevated amounts of ion 50) or a low-mass gain Electron Multiplier (for lower amounts of Ion 50). A dirty source is remedied by cleaning the ion source (and replacing the filaments). Problems with the rough pump can be resolved by changing the rough pump oil (be sure only to use Inland 45 oil) and/or replacing the beads in the molecular sieve filter on the rough pump (for Oil Diffusion Pump systems). If neither of these works, it's possible that the rough pump may need replacement.

Ion 75 (Acceptance criteria: 30-60% of mass 95); Affected mainly by the ratio of 69 to 131 and 219 in our tune file. Like ion 50, tests for adequate low-end sensitivity.

Tuning issues that cause problems with this ion:

Generally, if ion 75 fails it is because it exceeds the 60% maximum percentage criterion. I have never seen it fail because it is <30% of mass 95. Sometimes ion 75 does ends up above 60% of mass 95. This means that either the system is too sensitive at the low end or an indication that the source is getting dirty. To remedy this, first raise the relative ratios of 131 and 219 each by about 5%. This increase of the mid-range ends up making the low end less sensitive and will lower the amount of ion 75 that is generated. If this fails, continue to boost the relative ratio of 131 compared to 219. If this fails, try cleaning the ion source. If you need to make ion 131 and/or 219 above 60% for BFB to pass I would suspect a hardware problem exist.

Hardware issues that cause problems with this ion:
The most common hardware issues that cause failure of ion 75 would be a dirty source (especially if you have elevated amounts of ion 50 AND elevated amounts of ion 75), problems with the rough pump (also for elevated amounts of ion 75). A dirty source is remedied by cleaning the ion source (and replacing the filaments). Problems with the rough pump can be resolved by changing the rough pump oil (be sure only to use Inland 45 oil) and/or replacing the beads in the molecular sieve filter on the rough pump (for Oil Diffusion Pump systems). If neither of these work, it's possible that the rough pump may need replacement.

Note for EPA Method 524.2

2A. Ion 75 (Acceptance criteria: 30-80% of mass 95); Affected mainly by the ratio of 69 to 131 and 219 in our tune file. Like ion 50, it tests for adequate low-end sensitivity.

The EPA, in its infinite wisdom, widened the range for Ion 75 for method 524.2. I guess they figured since they're making you shoot a smaller amount of BFB (25 ng as opposed to 50 ng with 624/8260), they'll cut you some slack with the problematic ion 75. An upper limit of 80% makes it such that the source would have to be VERY dirty or some hardware problem would have to exist for it to fail.

Ion 95 (Acceptance criteria: Base peak, 100% relative abundance); Affected mainly by the ratio of 131 to 69 and 219 in our tune file.

Tuning issues that cause problems with this ion:

Generally, if ion 95 fails it is because ion 174 or 176 is the base peak. This means that ion 131 is too low and ion 219 is too high. To remedy this, raise the relative ratio of 131 and lower the relative ratio of 219 each by about 5%. This change will lower the 174/176 pair and should restore 95 to base peak status. If you need to make 131 greater than 219 by more than 15% for BFB to pass I would suspect a hardware problem might exist.

Hardware issues that cause problems with this ion:

If ion 95 fails it is because ion 174 or 176 is the base peak then the system might be running at below-ideal temperatures. In order to obtain proper ratios, the source and analyzer temperatures have to be correct. Be sure the system has thermally stabilized by allowing sufficient time (see discussion earlier in this issue). If they system has had enough time to thermally stabilize, then perhaps the analyzer is too cold. Use the following chart as a guideline:

MSD	Source temp	Quad temp	Transfer line temp
5970	200°C	same as source	250°C
5971	NA	NA	280°C
5972	NA	NA	280°C
5973	200°C to 230°C	150°C	280°C

Ion 96 (Acceptance criteria: 5-9% of mass 95); Affected mainly by the peak width of ions 69 and/or 131 in our tune file.

Tuning issues that cause problems with this ion:

Generally, if ion 96 fails it is because the peak width of ions 69 and/or 131 are not close enough to 0.50 amus. I have seen this isotope ion fail on both ends of the spectrum. If ion 96 falls below the 5% minimum, try narrowing the peak widths of ions 69 and/or 131. If ion 96 falls above the 9% maximum try widening the peak width of ions 69 and/or 131. Also, try lowering the abundance threshold and/or raising the Electron Multiplier setting.

Keep in mind that failure of this minor ion is often linked to poor peak shape in manual tune. So, even if the peak width is correct, you can still fail if the peak shapes of ions 69 and/or 131 are poor. I have seen many instances where elevated Entrance Lens settings distort the peak shape in Manual Tune. Sometimes, but not always, Entrance Lens settings above 100 mV/amu can cause distortion with the 5970, 71 and 72 and settings as low as 40 mV/amu can cause distortion with the 5973.

If this doesn't work, try changing the DC Polarity. For the 5970, this would be a small service issue as to do this one needs to swap 2 wires on the RFPA Board of the analyzer. For the 5971, 72 and 73, you can swap polarities in Manual Tune from POS to NEG (or vice versa). If you change Polarity, you'll need to do a peak width and mass axis calibration and retune the system as undoubtedly the ratios of 69-131-219 will change as well.

Hardware issues that cause problems with this ion:

If this issue can't be resolved by adjusting peak widths or changing polarities, a contaminated quadrupole and/or faulty electronics problem may exist. Usually, manual tune peak shape and corresponding isotope ratios are linked to problems with the RFPA (Radio Frequency Power Amplifier) electronics, so that would be the first thing to check.

You may also need to re-tune the RF coils to improve peak shape. This would be a service issue.

Ion 73 (Acceptance criteria: <2% of mass 174); Affected mainly by the peak shape of ion 219 in our tune file.

Tuning issues that cause problems with this ion:

This is an interesting one. Ion 173 should be absent or present in very small abundance. If it is found above the 2% of mass 174 level, it is usually because of poor peak shape in ion 219. Even if the peak widths are fine, ion 173 will fail if fronting occurs in ion 219 in Profile Scan. When tuning, you need to closely examine the peak shapes of all three ions, especially ion 219. If the peak shape of 219 is not Gaussian (symmetrical), ion 173 will be created at unacceptably high levels.

You can also try swapping the Polarity to see if peak shape improves. Also, be sure you have the Threshold set correctly in your acquisition method. It's possible that by raising the Threshold you may remedy this problem.

Hardware issues that cause problems with this ion:

The first thing to do is to clean the source, paying extra close attention to the Entrance Lens. The Entrance Lens is the component of the Ion Source that comes in contact with the quadropole, so contamination on the Entrance Lens can affect peak shape. For you 5970 users, it would be a good idea to swap Entrance Lenses if the white ceramic insulator looks excessively dirty .

Another possible remedy would be to clean the quadrupoles. (Warning: cleaning the quadrupoles is NOT considered routine maintenance as is cleaning the source and should only be done by trained personnel.)

Ion 174 (Acceptance criteria: 50-99% of mass 95); Affected mainly by the abundance of ion 219 relative to 69 and 131 in our tune file.

Tuning issues that cause problems with this ion:

I have seen this ion fail on both ends of the spectrum. If ion 174 is too large (i.e. it's the base peak), lower the relative abundances of both 131 and 219, especially ion 219. Try setting 131 about 5-10% greater than 219 in you tune file. Conversely, if ion 174 falls below 50% of mass 95, raise the relative abundances of both 131 and 219, especially ion 219. Try setting 219 about 5-10% greater than 131 in you tune file. Refer to the discussion a few pages back regarding ion 95 being the base peak.

Hardware issues that cause problems with this ion:

If ion 174 or 176 is the base peak then the system might be running at below-ideal temperatures. In order to obtain proper ratios, the source and analyzer temperatures have to be correct. Be sure the system has thermally stabilized by allowing sufficient time (see discussion earlier in this issue). If they system has had enough time to thermally stabilize, then perhaps the analyzer is too cold.

Tuning issues that cause problems with this ion:

This is a similar situation to ion 96, only ion 219 in our tune file is the key ion as opposed to 69 and/or 131. Generally, if ion 175 fails it is because the peak width of ion 219 is not close enough to 0.50 amus. I have seen this isotope ion fail on both ends of the spectrum. If ion 175 falls outside the 5-9% window, try widening or narrowing the peak width of ion 219. Try setting the peak width to 0.45 amu, then 0.50 amu, then 0.55 amu and finally 0.60 amu. You can accomplish this by raising or lowering the AMU gain and/or AMU offset. Also, adjusting the 219 Wid setting (for 5971, 2 and 3 MSDS) also can be adjusted. It's dangerous to set the peak widths much further from the 0.45-0.60
as this can cause the mass spec to mis-assign masses (i.e. it will not be able to reliably resolve one mass from another.)

You can also try swapping polarities.

If ion 175 is absent in some of the scans, you can also try changing the A/D setting (usually raising the setting helps this problem). Details of this are given in the next section.

If none of this works, faulty electronics and/or a contaminated quadrupole may exist.

Hardware issues that cause problems with this ion:

First, try cleaning the ion source.

Another possible remedy would be to clean the quadrupoles. (Warning: cleaning the quadrupoles is NOT considered routine maintenance as is cleaning the source and should only be done by trained personnel.)

Also, the rough pump plays a role in properly resolving this ion. Check the foreline pressure. For oil diffusion pump systems like the 5971, 5972 and some 5973s, this is reported on your Manual Tune report as Vacuum (expressed as millitorr). Foreline pressures above 60 mtorr can cause problems with the mass spec being unable to resolve Ion 75.

Ion 176 (Acceptance criteria: 95-101% of mass 174); Affected mainly by the abundance of ion 219 relative to 69 and 131 in our tune file.

Tuning issues that cause problems with this ion:

I have seen this ion fail on both ends of the spectrum. The problem is that there is no known remedy as far as adjustment of ratios or peak widths. The usual solution is to perform a 3-scan Enhancement (i.e. averaging of the Apex + -1 scan) or try either the Apex-1 or the Apex +1 scan. Often times a passing spectrum will result. If this happens only occasionally, then it was probably a fluke and I would just shoot BFB again-it'll probably pass. If it's a chronic problem, double check you A/D (Analog to Digital) setting (Also called Sampling rate on some systems). You might want to *increase* the A/D setting such that each scan on your peak is an average of more scans and is a more accurate representation of the true spectrum. Usually, megabore columns employ A/D of 2^3=8. Try 2^4=16 and see if the problem is solved. If you are using 2^2=4, try using 2^3=8 for your A/D.

Hardware issues that cause problems with this ion:

Often times, cleaning the Ion source will remedy this problem.

Ion 177 (Acceptance criteria: 5-9% of mass 176); Affected mainly by the peak width of ion 219 in our tune file.

Tuning issues that cause problems with this ion:

This is a similar situation to ion 175, although this ion is a lot less problematic. Generally, if ion 177 fails it is because the peak width of ion 219 is not close enough to 0.50 amus. I have seen this isotope ion fail on both ends of the spectrum. If ion 177 falls outside the 5-9% window, try widening or narrowing the peak width of ion 219. Try setting the peak width to 0.45 amu, then 0.50 amu, then 0.55 amu and finally 0.60 amu. You can accomplish this by raising or lowering the AMU gain and/or AMU offset. Also, adjusting the 219 Wid setting (for 5971, 2 and 3 MSDS) also can be adjusted. It's dangerous to set the peak widths much further from the 0.45-0.60 as this can cause the mass spec to mis-assign masses (i.e. it will not be able to reliably resolve one mass from another).

You can also try swapping polarities.

If none of this works, faulty electronics and/or a contaminated quadrupole may exist.

Hardware issues that cause problems with this ion:

First, try cleaning the ion source.

Another possible remedy would be to clean the quadrupoles. (Warning: cleaning the quadrupoles is NOT considered routine maintenance as is cleaning the source and should only be done by trained personnel.)

Summary of BFB Tuning

Usually ratios of 69-131-219 of 100%-37%-37% respectively and peak widths at 0.50 amu will cause BFB to pass...but NOT ALWAYS. Keep in mind that you need to make whatever adjustments are necessary to make BFB pass. Volatile systems are less dynamic that Semivolatile systems generally because the source stays cleaner (less contamination hits the detector on a purged sample than in a Methylene Chloride extract) so the drift is less frequent and less severe. But all GC/MS systems eventually show some change.

Attachment IV: Agilent Document: BFB Tuning for Environmental Analysis: Three Ways to Succeed.

BFB Tuning for Environmental Analysis: Three Ways to Succeed

Application

Environmental

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Abstract

The United States Environmental Protection Agency methods 524.2, 8260B, and Contract Laboratory Program Statement of Work employ purge and trap concentration of volatile compounds in water samples with analysis by gas chromatography/mass spectrometry. Each method requires the mass spectrometer to meet specific tuning criteria before proceeding to actual samples. This paper summarizes these tuning criteria, and shows three different ways that the Agilent Technologies 6890/5973 gas chromatograph/mass selective detector system can be tuned to meet them. A very simple and robust procedure is described in the Modified Autotune section. A quick reference guide for this procedure is given at the end of the paper under Modified Autotune Summary.

Introduction

If you are already familiar with 4-bromofluorobenzene (BFB) tuning and evaluation procedures, you may want to go directly to the section titled "Modified Autotune Summary" found at the end of this paper. It offers an alternative approach for tuning Agilent 6890/5973 GC/MSD systems that is routinely successful in this laboratory.

The United States Environmental Protection Agency (USEPA) has developed several methods for the analysis of volatile organic compounds (VOCs) in water samples. The three most widely used procedures all employ purge and trap (P&T) sample introduction followed by capillary column gas chromatography with mass spectral detection (P&T/GC/MS). USEPA Method 524.2 revision 4[1] is used for drinking water analysis while Method 8260B revision 2[2] is used for wastewater. The USEPA Contract Laboratory Program Statement of Work (CLP-SOW)[3] uses a similar P&T/GC/MS method for the analysis of hazardous waste.

There are many similarities among these three USEPA volatiles methods. One common requirement is that the GC/MS system must be tuned in such a way that 4-bromofluorobenzene (BFB) meets specific ion abundance criteria. This requirement helps to ensure that data are comparable between instruments of different design and

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among various laboratories. This paper summarizes USEPA method 524.2, 8260B, and CLP tuning criteria, and shows three different ways that the Agilent Technologies 6890/5973 GC/MSD system can be tuned to meet them.

Experimental

A standard containing fluorobenzene, 1,2-dichlorobenzene-d_4 and 4-bromofluorobenzene at 2.0 mg/mL was purchased from AccuStandard (New Haven, CT). A portion of this solution was diluted in methanol (B&J HPLC and pesticide grade) to a concentration of 50 ng/µL.

Standards for tune evaluation were injected by syringe or P&T into several different Agilent Technologies 6890/5973 GC/MS systems. When making syringe injections into the split/splitless inlet, a liner with a 900-µL volume was used and no more than 1.0 µL was injected to avoid over-expansion in the inlet.

Results and Discussion

Tuning Criteria

Table 1 lists the tuning criteria for USEPA methods 524.2, 8260B, and CLP-SOW. All three methods base their tuning criteria on the ion responses of BFB. All ion responses are reported relative to *m/z* 95, which is assumed to be the base peak even though ions 174 and 176 may be larger in the CLP-SOW method.

While many of the requirements in Table 1 are the same for all three methods, some important differences are worth noting. Method 8260B actually allows the analyst to use the tuning criteria specified in either of the other two methods. More importantly, it allows one to use "manufacturers tuning (sic) instructions" so long as it does not hurt method performance. However, many laboratories still follow the BFB tuning requirements specified in method 8260B or choose to substitute CLP-SOW tuning criteria.

Methods 524.2 and 8260 require that *m/z* 95 be the base peak in the BFB spectrum, which caps the *m/z* 174 relative abundance at 100% (relative to *m/z* 95). The CLP-SOW requirements allow *m/z* 174 to be up to 120% of *m/z* 95. Tuning procedures that reduce the response of *m/z* 174 too much may lead to lower overall sensitivity, especially for bromoform which has a quant ion of *m/z* 173. Conversely, maximizing this ratio, within the requirements of the method, can enhance overall sensitivity.

Automated BFB Tuning

The Agilent 5973 MSD uses perfluorotributylamine (PFTBA) for electron impact tuning because it exhibits good stability, the right volatility, and a wide range of fragment masses. However, USEPA volatiles methods evaluate the tune using BFB which produces an entirely different spectrum.

Table 1. Criteria for BFB Tuning for Three Capillary GC/MS Volatiles Methods

	Relative Abundance Criteria		
Mass (*m/z*)	Method 524.2	Method 8260B[a]	CLP-SOW
50	15 to 40% of 95	Same as 524.2	8 to 40% of 95
75	30 to 80% of 95	30 to 60% of 95	30 to 66 % of 95
95	Base Peak, 100%	Same as 524.2	Same as 524.2
96	5 to 9% of 95	Same as 524.2	Same as 524.2
173	<2% of 174	Same as 524.2	Same as 524.2
174	>50% of 95	Same as 524.2	50 to 120% of 95
175	5 to 9% of 174	Same as 524.2	4 to 9% of 174
176	>95 to <101% of 174	Same as 524.2	93 to 101% of 174
177	5 to 9% of 176	Same as 524.2	Same as 524.2

[a]Alternative tuning criteria may be used (for example, CLP or Method 524.2) including manufacturer's instructions provided that method performance is not adversely affected.

Therefore, automated (or manual) tuning procedures must adjust PFTBA ion responses in order to get the desired BFB response ratios. Agilent G1701CA EnviroQuant ChemStation software automates BFB tuning so that the instrument typically passes the more restrictive USEPA Method 524.2 and 8260B requirements listed in Table 1. After tuning, the analyst must inject a BFB standard by syringe or P&T to verify that the tune passes the requirements for the method in use.

Automated BFB tuning adjusts MSD source parameters so that PFTBA ion abundances meet predetermined "targets." The default PFTBA target values are set so that a subsequent BFB injection should meet the requirements for all three methods. Table 2 shows a portion of a BFB tune report that includes the target responses (as a percentage of *m/z* 69) for *m/z* 50, 69, 131, 219, 414, and 502. The actual abundances achieved by the tune are shown on the last line. When these targets are met, the Agilent 5973 MSD normally passes any of the tuning criteria listed in Table 1.

Table 2. A Portion of a Typical BFB Tune Report

Target Mass:	50	69	131	219	414	502
Target Abund (%):	1.0	100.0	45.0	55.0	2.4	2.0
Actual Tune Abund (%):	1.2	100.0	48.1	59.3	2.7	2.3

Figure 1 shows an average spectrum obtained for a 1-µL manual injection of BFB (50 ng/µL split 50:1) using the tune shown in Table 2. Agilent G1701CA EnviroQuant ChemStation Environmental Data Analysis software can evaluate the spectrum automatically and generate a report that is archived with the data file. Because BFB tuning criteria are not uniform among USEPA methods, the analyst must first specify the allowable ranges using the form shown in Figure 2. The form is accessed in Environmental Data Analysis by selecting Tuner/Edit BFB Criteria on the dropdown menu.

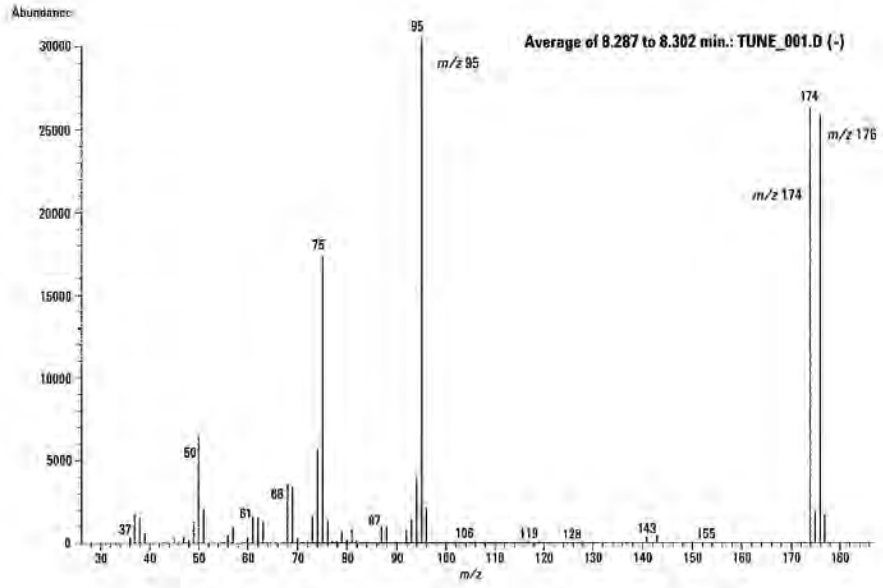

Figure 1. Average spectrum of BFB after performing a standard BFB automated target tune. One µL of a methanol solution containing 50 ng/µL of BFB was injected by hand.

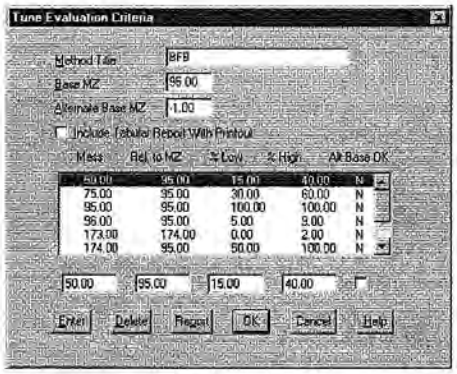

Figure 2. The Agilent G1701CA EnviroQuant ChemStation screen for entering BFB tune criteria. The user can modify the parameters to meet the requirements of the method in use. These values are used by the ChemStation for automated tune evaluation.

Having entered abundance criteria for the method in use, one can automatically assess the suitability of the tune using the EnviroQuant software (Figure 3). One can choose to "Evaluate BFB to Screen/Printer" in which case it will evaluate the current spectrum. This can be a single spectrum or an average. Alternatively, by choosing "Autofind BFB to Screen/Printer," the software automatically finds BFB in the chromatogram, averages the top three spectra and subtracts a baseline spectrum. In either case, a report such as the one in Figure 4 is generated. The most recent report is archived in the datafile.d directory in a file called tuneeval.txt.

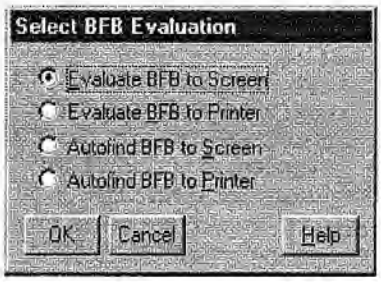

Figure 3. Choices for automated BFB tune evaluation by the EnviroQuant software. The "Evaluate BFB..." choices use the spectrum (single or averaged) in Data Analysis window 1 for evaluation. The "Autofind..." choices automatically find the BFB peak, average the top three BFB spectra and subtract a baseline spectrum prior to evaluation.

BFB

Data File : C:\HPCHEM\1\DATA\Sep24_01\TUNE_001.D Vial: 1
Acq On : 24 Sep 2001 2:25 pm Operator:
Sample : BFB for tuning 1 uL Inst: GC/MS Ins
Misc : Multiplr: 1.00
MS Integration Params: rteint.p

Method : C:\HPCHEM\1\methods\envdef.m (RTE Integrator)
Title :

AutoFind: Scans 1567, 1568, 1569; Background Corrected with Scan 1559

Target Mass	Rel. to Mass	Lower Limit%	Upper Limit%	Rel. Abn%	Raw Abn.	Result Pass/Fail
50	95	15	40	21.6	6769	PASS
75	95	30	60	56.5	17708	PASS
95	95	100	100	100.0	31317	PASS
96	95	5	9	7.1	2209	PASS
173	174	0.00	2	0.0	0	PASS
174	95	50	100	82.8	25933	PASS
175	174	5	9	7.4	1910	PASS
176	174	95	101	99.3	25747	PASS
177	176	5	9	6.6	1702	PASS

TUNE_001.D envdef.m Mon Sep 24 16:00:27 2001 MSVOC04

Figure 4. The Agilent EnviroQuant ChemStation BFB Tune Evaluation Report for the spectrum shown in Figure 1.

In this case the automated BFB tuning procedure produced a tune that passes Method 524.2 and 8260B criteria with a 174/95 ratio of 82.8%. This ratio is limited to 100% by these USEPA methods, which specify that *m/z* 95 must be the base peak. To meet these strict guidelines, one has to "de-tune" the Agilent 5973 MSD which results in somewhat lower instrument sensitivity. Laboratories may want to increase the 174/95 ratio so it more closely approaches the 100% limit of Methods 524.2 and 8260B or so that it approaches the 120% limit specified in the CLP-SOW method. Most laboratories that perform Method 8260B tune their instruments to meet the CLP-SOW requirements because the method allows laboratories to use these tune criteria and the MSD performance is closer to optimum.

In addition to the automated BFB tune, there are two procedures that can be used to improve instrument sensitivity, to meet the more liberal CLP-SOW requirements, or to create a passing tune should the standard BFB autotune fail. In this laboratory, the "Modified Autotune" procedure was found to produce tunes that routinely passed BFB criteria for any of the three methods. As shown below, changing the BFB tuning targets can also produce a passing BFB tune while enhancing the signal for bromoform.

Target Tuning

Automated BFB tuning adjusts MSD source parameters to achieve the target responses required for the method in use. This is essentially a "target tune" procedure where the initial target abundances provided by the software are designed to

meet the more restrictive 524.2 and 8260B requirements. When needed, it is easy to change the target PFTBA relative abundance criteria to produce the desired affect on the BFB ions. This is done by selecting View/Manual Tune/Set Tune Targets.

For example, consider the spectrum in Figure 1 which passed all of the tuning criteria, but which had a lower than optimum *m/z* 174 response. Experience in this laboratory has shown that increasing the relative abundance of *m/z* 174 will increase the overall sensitivity of the instrument, in particular for the bromoform response at *m/z* 173. As shown in Figure 5, the target abundances for ions 131 and 219 were each increased to 70% from their default values of 45% and 55% respectively. These choices were saved to the BFB.U tune file and a new BFB Target Tune was run. Figure 6 shows the new BFB spectrum (average of three spectra across the apex with baseline subtraction) which passes CLP-SOW criteria (Table 1) and is, therefore, satisfactory for either CLP or 8260B volatiles methods.

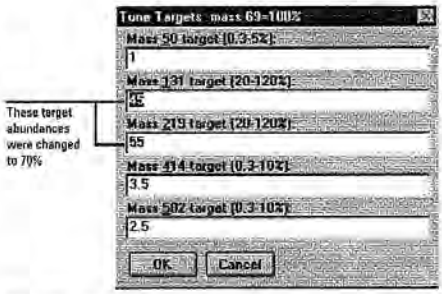

Figure 5. PFTBA target abundance values (relative to *m/z* 69) used for "target" tuning. When these abundances are saved to the BFB.U tune file, they are used by the BFB target tune algorithm.

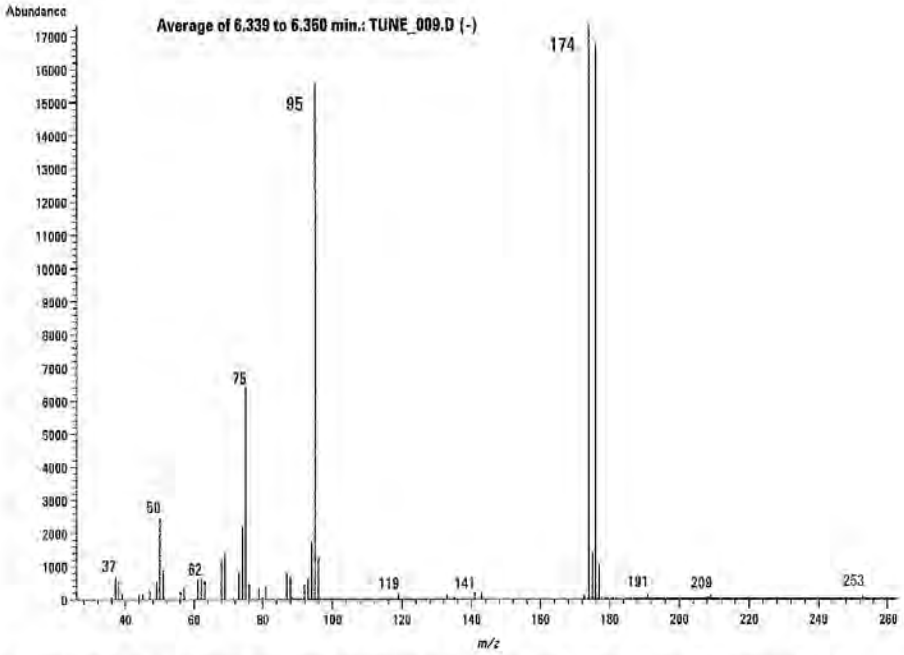

Figure 6. Average BFB spectrum obtained by changing the tune targets for *m/z* 131 and 219 to 70% (relative to *m/z* 69). This spectrum passes CLP-SOW tuning criteria.

Modified Autotune

With the convenience of automated tuning procedures available in the Agilent ChemStation software, most analysts have gladly given up the idea of manually tuning their 5973 MSDs. A combination of automated tuning with a slight manual modification has given excellent BFB results in this laboratory. The total process is easy and usually takes just a few extra minutes after the autotune is complete. The steps are described below and are summarized in a "quick reference" format in the next section.

1. From the Manual Tune portion of the software, perform an Autotune (select Tune/Autotune). This algorithm tunes the Agilent 5973 MSD for maximum sensitivity over the entire mass range and is widely used by methods that do not specify other tune criteria. This autotune emphasizes overall sensitivity by improving abundances for higher mass ions (for example, 502). As a result, the Autotune procedure typically gives an abundance for *m/z* 50 that is too low to meet 524.2 and 8260 criteria and an abundance of *m/z* 174 that may be too high, even for CLP-SOW tuning.

2. After completing the Autotune procedure, choose Edit MS Params (under the AdjParam menu item) which will display the screen shown in Figure 7.

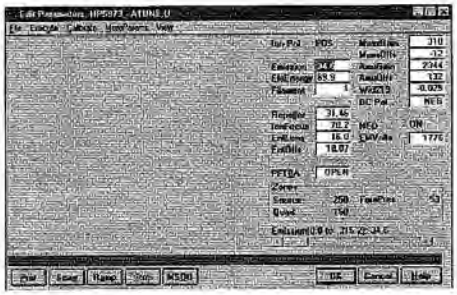

Figure 7. The Edit Parameters screen found by selecting AdjParam/Edit MS Params in the main Manual Tune window.

3. Two changes are required in the default values used for adjusting parameters in this view. First, under the MoreParams menu, choose Ramp Params and change the "Stop" value for the ion focus to 140 as shown in Figure 8. Close this window and choose AcqParams under the MoreParams window and change Mass 3 from 502 to ion 50 as shown in Figure 9. Close this window and return to the main Edit Parameters screen (Figure 7).

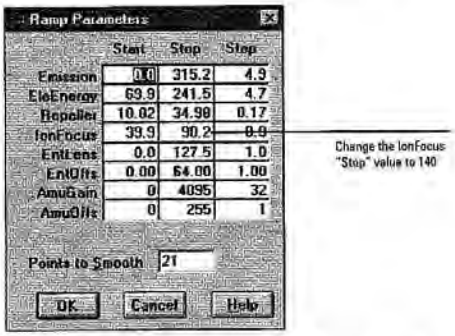

Figure 8. This window allows the user to set ranges for the various tuning parameters. The default ion focus "Stop" setpoint of 90 was set to 140.

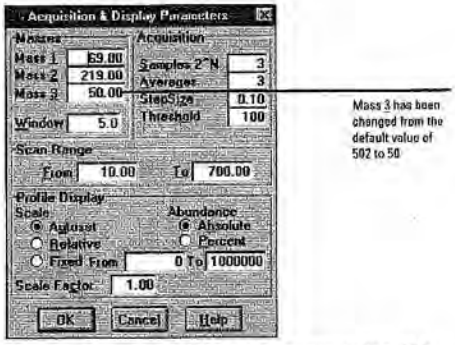

Figure 9. Acquisition and Display Parameters window. *M/z* values of 69, 219, and 50 have been chosen so that these responses can be ramped and their relative abundances displayed.

4. Highlight the IonFocus window with the cursor and then select Ramp. This gradually ramps the ion focus voltage over the specified range while monitoring the response of ions 69, 219, and 50. After about a minute, a plot of these ion responses vs. the ion focus voltage appears in the window (Figure 10).

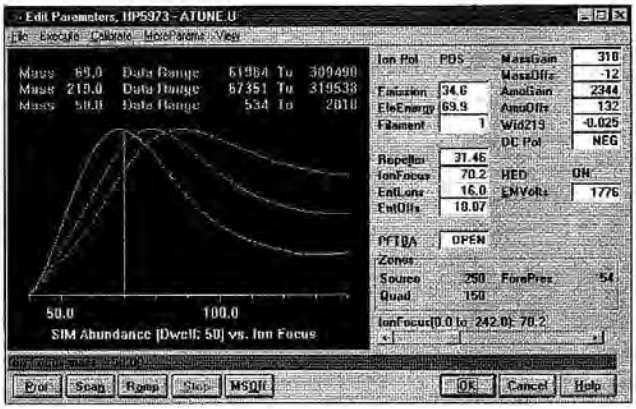

Figure 10. Abundances for ions 69, 219, and 50 while ramping the Ion Focus from 40 to 140.

5. Under the View dropdown menu item, choose Expand. This view shows the current Ion Focus setting, the abundance of m/z 69 and the relative abundances of ions 219 and 50 (Figure 11). From the plot, it is easy to see that an increase in the Ion Focus value should increase the 50:69 ratio while reducing the 219:69 ratio. These are exactly the changes that should enable the MSD to pass BFB tuning criteria.

   Note that the ion focus ramping procedure can also be performed from the main Manual Tune screen by choosing Ramp/Ramp Ion Focus on the dropdown menu.

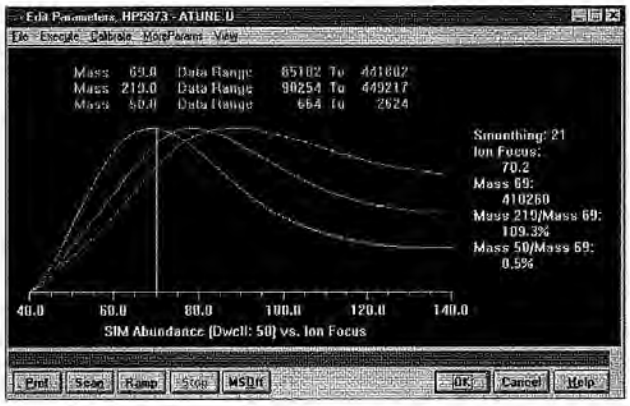

Figure 11. An expanded view of the SIM-Abundance-vs-Ion Focus plot obtained by selecting View/Expand. This view allows one to drag the vertical line to different setpoints while observing changes in the ion relative abundances.

6. The vertical line indicates the current ion focus setpoint. Use the cursor to drag this setpoint line to the right while observing the change in the 219:69 and 50:69 ratios. Agilent laboratories have had good success by setting the Ion Focus to values between 100 and 135 V. This should result in a 219:69 ratio in the 60-80% range and a 50:69 ratio that is 0.8 or greater. If tuning to meet 524.2 requirements, the 219/69 ratio should be on the low side of this range.

   An alternative to the above procedure is to select Scan in the Edit Parameters window (Figure 7) while monitoring ions 69, 219, and 50. The 219:69 and 50:69 ratios are displayed under the Relative Abundance heading and are updated with each scan. Highlight the Ion Focus setting and adjust its value using the slider bar. The effect of different Ion Focus values will be seen almost immediately in the ion ratios. These ratios will bounce around somewhat, but trends can be seen over a few scans. A good choice for the 50:69 ratio would be about 0.85.

7. Click OK and return to the Manual Tune screen. Under the Calibrate menu item, choose Adjust Abundances, which will automatically reset the electron multiplier to get ion abundances in the optimum range. Save the tune, choosing a new name for the tune file (for example, BFB1.U). Return to Instrument Control (View/Instrument Control) and be sure to select this tune file for the method used to acquire the BFB checkout chromatogram. Inject or purge an appropriate amount of BFB and evaluate the tune using the software tools provided (Figures 2 through 4). Assuming that it passes, assign this tune to the P&T/GC/MS volatiles method in use.

Figure 12 shows the spectrum (average of the three scans across the apex with baseline subtraction) for a 1-µL syringe injection (50 ng/µL split 50:1) of BFB using an ion focus value of 115 V. All other parameters (except for the electron multiplier) were set by the Autotune algorithm. This spectrum passes any of the tuning criteria listed in Table I but has a higher 174/95 ratio than was achieved using the standard BFB tune.

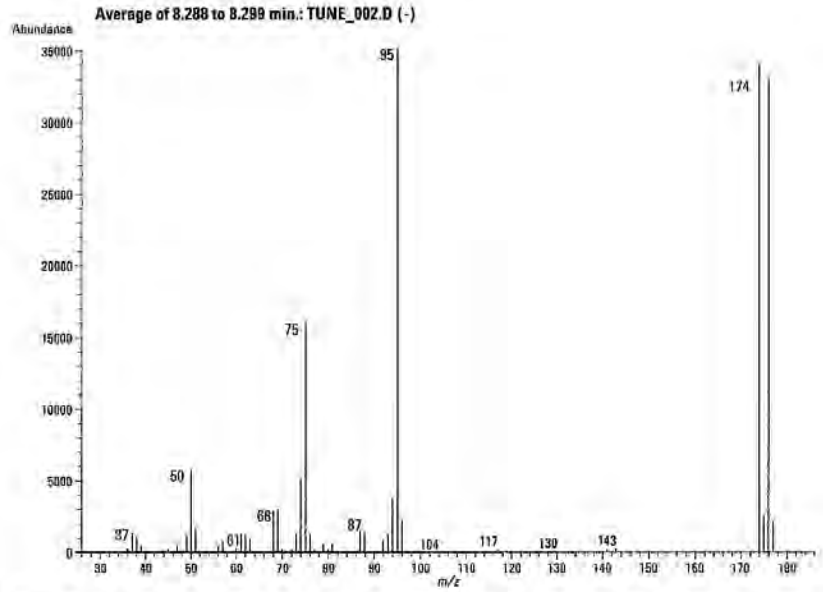

Figure 12. Average spectrum of BFB obtained after using the procedure described under Modified Autotune. After running a standard Autotune, the Ion Focus value was increased to 115 V.

The true test of a successful BFB tune is whether it holds up during repetitive VOC analyses and through normal instrument maintenance procedures. In one extreme test, the same BFB tune easily passed CLP-SOW criteria during a period when two different MSD sources were installed and four different filaments were used. On one Agilent 6890/5973 GC/MS instrument this procedure did not work until the MSD source was cleaned.

Finally, a note of caution is appropriate. While these techniques have worked well for the Agilent 6890/5973A and N GC/MSD systems, this does not imply that the same procedures are appropriate for older Agilent MSDs. Tuning frequency is dictated by the nature of the samples, choice of column and other factors such as column bleed and source cleanliness. If the source becomes too dirty, it must be cleaned in order to pass BFB tuning criteria, no matter which approach is taken.

Modified Autotune Summary

These steps summarize the procedure for modifying the standard Agilent 5973 Autotune to pass BFB tuning criteria. It is provided here as a quick reference guide for those who are already familiar with tuning procedures.

1. In the Manual Tune portion of the Agilent GC/MS ChemStation software, perform a standard Autotune.
2. In the Ramp Parameters window, change the Ion Focus Stop value to 140.
3. In the Acquisition & Display Parameters window, change ion 502 to 50.
4. In the Edit Parameters window click on Ion Focus and then on Ramp.
5. Adjust the Ion Focus value so that the 50/69 ratio is 0.8 or larger. The 219/69 ratio usually falls in the 60 to 80% range. When this PFTBA ion ratio is under 70%, the 174/95 ratio of BFB is usually under 100%.
6. In the Manual Tune window under the Calibrate menu item, adjust ion abundances.
7. Save the tune file with a new name, assign it to the method and verify that the tune passes by injecting a BFB sample according to the method requirements.

Conclusions

There are several ways to tune the Agilent 6890/5973 GC/MSD system to meet any of the USEPA BFB tuning criteria. However, factors such as source cleanliness, choice of column, flow rates and instrument-to-instrument variability make each GC/MSD system unique. Automated BFB and target tuning procedures are normally successful but the 174/95-ion ratio may not be high enough to meet laboratory needs. In our experience, the most robust and long-lasting BFB tunes were generated by the procedure outlined above under Modified Autotune. The procedure takes just a few minutes to complete.

References

1. *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry*, Method 524.2, revision 4.1, U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Cincinnati, OH (1995).
2. *Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)*, Method 8260B, revision 2 (1996).
3. *USEPA Contract Laboratory Program Statement of Work for Organics Analysis, Multi-Media, Multi-Concentration, OLM04.2*, USEPA Contract Laboratory Program, Office of Emergency and Remedial Response.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

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Agilent Technologies

Attachment V

Pace Analytical Services, Inc
1241 Bellevue Street Suite 9
Green Bay, WI 54302
Phone: 920 469 2436
Fax: 920 469 8827

VOA Calibration Process

Epic Pro

Make Q-Batch

- Batching -> New Batch -> Queue = MSV
- Click Empty Batch icon on taskbar
- Highlight QC Rule -> F9 -> type MSV
- Select appropriate QC Rule (i.e. MSV water) – Select OK – F10 to save
- Record Q Batch #

Create Standards

- System -> Utility -> Clone Standard by Event
- Select Event (111 = MeOH soil curve, 115 = Water/LLsoil curve) Select OK
- Double Click on standard event
- Review Standard composed of – Find/Replace if necessary
- Update expiration date to 7 days from creation – F10 to Save
- Operations -> Standard Log -> Enter – Record Standard #'s

Chemstation

Create Chemstation methods

- Tune MS, Save Tune file as date (i.e. 072513.u)
- Update both DBFB and Curve method to use new tune file
- Save Curve method as date (i.e. W072513.m)

Set up Sequence

- Load pre-existing curve sequence if available
- Change old method to the new method & copy through all files (DBFB remains the same)
- Change Q-Batch# in BFB, Curve and ICV files

Start Analysis

- Run minimum of 2 BFB injections to ensure the tune is optimized
- Retune or adjust as needed, repeat 2 more BFB
- Analyze a 2 blanks to verify the system is clean and IS areas within range
- First IS, pentafluorobenzene should be between 300,000 – 550,000 area counts
- Raise or lower EM as necessary – You ***Must*** reanalyze BFB if voltage was adjusted
- Reanalyze blanks to ensure correct voltage and proceed w/ analysis of curve

Target

Create Method

- Rename existing method to new name matching Chemstation method (i.e. W072513.m)
  Note: if other data in Directory was processed w/ old method a copy of that method must remain in directory as well.
- To avoid excessive file size, Audit trail in method should be reset at a minimum of annually
  The ***ONLY*** time an audit trail may be rest is prior to calibrating the instrument.
  Note: The Audit trail will remain intact in previous days folder.
  Double click into method folder, highlight the .audit file and delete

Edit Method

- Security -> Method unlocked
- Global -> Calibration – click "update Curve Parameters" to averaged
- File -> Zero Calibration
- Compound ->Edit Compound -> Calibration
  Review all analytes to ensure all necessary points are enabled
  Are any 300 points dropped? If so, mark them enabled and make note of these to change the "Max Compound Amount Limit" after the curve has been run.
- Reports -> Tabular –> "Print Custom Report" –click "Select Format"
  On toolbar a "Select" icon will appear
  Click on ManIntprepost.mac – click "Open"
  Note: It is necessary to do this ***Every*** time a calibration is zeroed, even if the macro shows up in this field as the link to the macro that was lost when the calibration was zeroed.
- Sample -> Default Sample
  Change "Lab Prep Batch" field to the new Q-Batch #
  Change "Client SDG" to be the instrument and date (i.e. 40MSV2-07252013)
- Sample -> Surrogate/ISTD Parameter
  Confirm that the correct IS/SS standard # is entered in the "Surrogate Lot#" field
  Example – 51970:1.163 The 51970 is the IS/SS number followed by a colon followed by the volume added (this is a fixed amount unless change to the standard delivery has occurred.)
- File -> Save Method
- File -> Exit

Process and Review Curve Data

- If significant Column maintenance was performed, it may be beneficial to process the 20 or 50 point first to update RT's as the larger concentrations will have better spectra to confirm correct identification
- Select Method to calibrate and process files
  Compound Sublist should be "all.sub"
  Sample Type change to Calib Sample
  Cal Level change to appropriate level 1-7
  Double check that the Q-Batch # in MiscInfo and Lab Prep Batch are correct and match
  Double check that the Client SDG reflects the instrument and date

- Review Target Data
  - Review each analyte of all points for correct spectrum, RT and appropriate integration
  - All Manual Integration of all curve points and ICV need to have Review Codes added
  - After reviewing all points, review each analyte point 1->7 to ensure consistent RT, spectra and Integration (i.e. shoulders cropped or included, etc.)

Review Curve in Target Method

- Edit Method
- Edit Compound -> Calibration
- Review each analyte to ensure Initial Calibration %RSD are less than 15.0%.
  - Note analytes >15% and re-examine target data for proper integration
- Check that all CCC compounds are less than 30% RSD
  - CCC's are11DCE, chloroform, 12DiChloropropane, toluene, ethylbenzene and vinyl chloride
  - Instrument maintenance must be performed to correct problem if any >30%
  - If %RSD >15% and <30% note %RSD to record later.
- Check that all minimum relative response factors (RRF) were met for the SPCC – Chloromethane, 11DCE, bromoform are 0.1 and 1122PCA, chlorobenzene are 0.3– if any %RSD >15 note RRF to record later.
- If %RSD > 15 – Drop Upper or lower point to achieve %RSD < 15
  - If the Report Limit (RL) for analyte is not the 1 point, can the 1 point be disabled
  - Can the 7 point be dropped (or 6 & 7 points) – **Will require lowering Max Amount
  - Note: ONLY upper or lower points can be dropped, ***NEVER*** an intermediate point!!
  - Must have minimum of 5 points for Averaged RF curve
  - After disabling appropriate points – Click "Update Calibration" button
- If %RSD still > 15 – Switch Curve fit to Linear Regression
  - Change curve fit to Linear
  - **CCC Compounds (11DCE, chloroform, 12dichloropropane, toluene, ethylbenzene, vinyl chloride) MUST still be <30% RSD.
  - Initial Calibration R^2 must be 0.990 or greater
  - Must have minimum of 5 points for Linear regression curve
  - b intercept should be as close to zero as possible
    - i.e. by dropping the 300 point does the intercept go from 0.1980442 -> 0.0681234
    - This will give less false positive hits but require linear range to be lowered to 200ug/L
- If R^2 is not > 0.990
  - Change curve fit to Quadratic
  - ***Must have minimum of 6 points**
  - R^2 must be 0.990 or greater
  - Like Linear regression the 300 point can be dropped (or 1 point added if RL is 5ug/L) to achieve the intercept closest to zero, as long as 6 points remain and linear range is adjusted.
- If calibration for compound will not pass
  - The Instrument cannot be run for lists including these analytes
  - Document analytes as failing in Run logbook
  - Place Post-It-Note on Instrument Terminal to alert other analysts of failures

Update Linear Range

- After all analyte curve fits have been checked
  - Compound->Edit Compound->Report Parms
  - Adjust "Max Compound Amt Limits" to reflect highest point used (300->200 if 7th point was dropped)
- Sublists -> Update Sublists
  - Check the "Update Sublists QC Limits" box
  - Highlight first sublist and hit Enter button
  - Arrow down to the next sublist and hit Enter
  - Repeat for all Sublists
  - **If you fail to update all the sublists, detects above linear range will not be "a" flagged in target
    - Epic Pro uses the "a" flag to switch Condition Code from "OK" to "OR"

Lock Method

- Security -> Initial Calibration Locked
- Note: Do not select "Method Locked" – This would not allow the method to be used to process data

Verify Initial Calibration

- View -> Initial Calibration
- This generates a report with calibration data that will appear on the lower tool bar
- Print report and review
  - The Calibration File Names in the header match the ***correct*** files used in the curve
  - All Average Response Factors < 15% and at least 5 points were included
  - All Linear Regression > 0.990 and at least 5 points were included
  - All Quadratic > 0.990 and at least 6 points were included
  - Are all low points dropped below Report Limit for that analyte
  - Any high points dropped verify that the Max on Column was lowered and Record max amount on the report
  - No midpoints of curve are missing
  - All CCC compounds averaged – If not is the %RSD < 30% - Record actual RSD on report
  - All SPCC minimum RF factors met – If not averaged, switch to Averaged in method record the RF on the report and switch curve back to appropriate curve fit
- Manually check individual Response Factors (RF) for at least one analyte
  - Calculate the RF for each point in the curve of an Averaged curve fit using the following formula
  - RF = (Area of analyte *concentration of IS) / (Area of IS *concentration of analyte)
- Save method and Exit

Re-quantify and Uploading Curve and ICV

- Select Method
- Highlight Curve and re-quantitate
- Process ICV – Must use all.sub (or Full.sub)

- Review ICV and check CLP.rp
  - All SPCC Minimum RF must be met (if analyte is linear, must hand calculate)
  - All CCC Analytes must be <20%
  - All other analytes must be <30%
    - Note: Up to 5% (5 Analytes for a full list spike) may be between 30-40%)
  - All Analytes > 40% will be flagged as failing
    - Document analytes as failing in Run logbook
    - Place Post-It-Note on Instrument Terminal to alert other analysts of failures
- Generate all files to paperless (BFB, Curve and ICV)
- Upload all files to Epic Pro (double check Q-Batch is correct prior to upload)
- Check Q-Batch in Epic to ensure Curve, BFB and ICV imported correctly (may take several minutes)

MN Low Standard Verification

- Copy 1ppb, 5ppb & 20ppb files into another folder (i.e. the unprocessed blank following 300ppb)
- Paste all 3 files than Rename example (07251305.D -> MN01-07251305.D)
  - This will allow original files to be un-manipulated
- Cut files and paste back in original folder
- Re-Quant new MN files as LCS
  - Sample Type = QC Control Sample
  - Click QC SampleType
    - Sample Type = LCS
    - Spike List = MNLOW1.spk, MNLOW5.spk, MNLOW20.spk
- Highlight all 3 files and Do Quick Forms – Form 3 of LCS
- Print Form 3's and pass on to Supervisor to update MN report limits in Epic Pro

Before proceeding with analysis of samples

- Check Chemstation sequence that correct Q-Batch is in BFB and CCC
- Check that correct Method is referenced in the sequence

Attachment VI

Pace Analytical Services, Inc
1241 Bellevue Street Suite 9
Green Bay, WI 54302
Phone: 920 469 2436
Fax: 920 469 8827

VOA Calibration Review Checklist

Method:	SW846 8260B
Instrument:	
Q-Batch:	
HBN:	

Comments: Check box if there is an issue and document what was done.

	Prior to Running Curve	*Comments:*
☐	IS/SS filled with Fresh standard and primed	
☐	Sparge tube/sipper tube clean or replaced	
☐	Replace Injection Port Septa if necessary	
☐	Instrument was tuned and new unique Tune file was created (i.e. 072513.u)	
☐	DBFB method was updated to use current tune file	
☐	Water method was updated to use current tune file and saved as the date (i.e. W072513.m)	
☐	Correct Q-Batch entered in sequence	
☐	Correct standards entered in sequence	
☐	Correct Method entered in sequence	

	Prior to Processing Curve in Target	*Comments:*
☐	Method renamed to match Chemstation Method name	
☐	Method Unlocked and Zeroed	
☐	All point enabled (if 300 point was previously dropped)	
☐	All compounds curve fit re-set to Averaged	
☐	Manual Integration Macro selected	
☐	Q-Batch entered in Method and BFB default sample in the Lab Prep Batch field	

	Prior to Processing Samples	*Comments:*
☐	Initial Calibration Report reviewd by another Analyst	
☐	Curve and ICV Passed - all failures recorded in logbook and note placed on instrument terminal	
☐	Sublist all updated to reflect linear ranges if 7th points were added or dropped	
☐	Files uploaded and generated to paperless	
☐	Q-Batch reviewed in EpicPro to assure properly imported	
☐	MN Low Standard re-quanted and Quick Forms generated	
☐	Correct Q-Batch and Method are in new sequence	

Issues: Write any and all out of control issues below:

☐ Labtrack was issued _____

☐ Supervisor was notified _____

To the best of my knowledge, all of the above information is correct and all supporting documentation has been provided.

Analyst: _____ **Date:** _____

Reviewer: _____ **Date:** _____

Pace Analytical Services, LLC
1700 Elm Street SE, Suite 200
Minneapolis, MN 55414

Phone: 612-607-1700
Fax: 612-607-6444

STANDARD OPERATING PROCEDURE

ANALYSIS OF WHOLE AIR SAMPLES FOR VOLATILE ORGANIC COMPOUNDS BY GC/MS

Reference Methods: EPA Compendium Method TO-15/TO-14

Local SOP Number:	S-MN-A-013-Rev.20
Effective Date:	Date of Final Signature
Supersedes:	S-MN-A-013-Rev.19

APPROVALS

Laboratory General Manager — Date: 23Dec2016

Laboratory Quality Manager — Date: 23 Dec 2016

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date

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TABLE OF CONTENTS

SECTION **PAGE**

1. PURPOSE/IDENTIFICATION OF METHOD

1.1. The purpose of this Standard Operating Procedure (SOP) is to provide quality control and analytical guidance for the analysis of whole air samples and soil vapor samples contained in Summa ® passivated canisters, Silco ® lined canisters (or equivalent), or sampling bags using gas chromatography/mass spectrometry. This SOP is based on Environmental Protection Agency (EPA) Compendium Method TO-15/14.

2. SUMMARY OF METHOD

2.1. Samples are received in Summa ® canisters or Silco ® lined canisters (or equivalent). The gauge pressure upon arrival is measured and recorded. The canister is then pressurized to 5 psi gauge pressure using an inert gas. The canister is connected to an autosampler tree, which concentrates the sample prior to injection into a GC/MS. The data is then analyzed for the desired volatile organic compounds.

2.2. This method addresses an extensive set of VOCs by incorporating a multisorbent, dry purge technique for water management.

2.3. An aliquot of the whole air sample is concentrated prior to gas chromatographic (GC) separation and mass spectrometry (MS) full scan detection. Samples expected to contain VOCs in a range of 0.1 parts per billion by volume (ppbv) to 500 ppbv can be analyzed by this technique.

2.4. If samples are received in sampling bags, see section 7.0 for appropriate holding times and actions to transfer the samples to a Summa ® canister to complete analysis as described in this SOP.

3. SCOPE AND APPLICATION

3.1. Personnel: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method.

3.2. Parameters: This procedure is designed to analyze whole air samples collected in Summa ® canisters, Silco ® lined canisters (or equivalent), or sampling bags for some of the volatile organic compounds (VOCs), or hazardous air pollutants (HAPs), found in Title III of the Clean Air Act Amendments of 1990. This SOP is related to only those VOCs that have been found to be stable when collected in Summa ® polished stainless steel canisters, Silco ® lined canisters or sampling bags (or equivalent). VOCs are defined as organic compounds having a vapor pressure greater than 10-1 Torr. Attachment I lists target VOCs applicable to this method.

3.3. This SOP is based on the EPA Compendium Method TO15 which can also be applied to TO14. As such, this SOP serves to cover both analyses. See EPA Compendium Method TO15 Section 3 and Attachment I for compound list.

3.4. For Ohio VAP, if requirements specified in this SOP are not meant, Pace Analytical will narrate any potential bias or justification in the project narrative on the final report. Additional narratives are provided as needed. Pace may have the need to narrate potential bias in the event of instrument failure, limited sample volume, report revisions or matrix interferences.

4. APPLICABLE MATRICES

4.1. This SOP is applicable to whole air samples and soil vapor samples contained in Summa ® passivated canisters, Silco ® lined canisters (or equivalent), or sampling bags using gas chromatography/mass spectrometry.

5. LIMITS OF DETECTION AND QUANTITATION

5.1. The most current reporting and detection limits can be found in the Laboratory Information Management System (LIMS).

6. INTERFERENCES

6.1. Carrier gas potentially contains small amounts of contaminants and is filtered prior to use in instrumentation. Other interferences are sample specific and are dealt with as they occur.

6.2. Interferences in samples can result from contamination of the canisters. To minimize this problem, processes must be implemented to ensure that the canisters are contamination free. See SOP S-MN-A-004 - Procedure for Cleaning, Certification, Leak Checking, and Preparation for Shipment of SUMMA Passivated Canisters, or equivalent replacement.

6.3. Contamination of analytical equipment can also occur when samples containing high concentrations of VOCs are analyzed. The resulting "carryover" contamination varies from system to system. The analyst needs to use best judgment when evaluating sample data following samples with large detection levels.

7. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

7.1. Collection, Preservation, Storage and Holding Time Table

7.1.1. The holding time indicated below is the maximum allowable time from collection to analysis per the analytical method. If the samples fail to meet the holding time, data will be qualified accordingly on the analytical checklist and on the final report with the appropriate footnote.

7.1.2. Note For Ohio VAP: As applicable, to the best of the laboratory's knowledge, if holding times are not met the laboratory will qualify the data accordingly indicating the bias present due to the exceedance.

Sample type	Collection per sample	Preservation	Storage	Hold time
Air	Samples are collected into evacuated Summa ® canisters, Silco ® canisters (or equivalent). The canisters are then shipped back to Pace Analytical Services, Inc. for analysis.	None	Ambient sample storage	Samples collected in Summa ® canisters, Silco ® canisters (or equivalent) must be analyzed within 28 days from collection. Samples collected in Minnesota are to be collected in canisters and must be analyzed within 14 days of collection per the Minnesota Pollution Control Agency (MPCA). If samples have been collected in bags, the samples need to be transferred to a Summa Canister within two days to maintain a 28 day holding time. The holding time is potentially extended to 72 hours per client specific QAPPS. Collection in a bag results in higher reporting limits. See Attachments VIII-X for instructions and documentation for the transfer procedure. Ohio VAP samples must be transferred to a Summa Canister within two days from collection to extend the holding time of collection to analysis to 28 days.

8. DEFINITIONS

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

8.2. Absolute canister pressure = Pg + Pa, where Pg = gauge pressure in the canister (kPa, psig) and Pa= barometric pressure.

8.3. Absolute pressure - Pressure measured with reference to absolute zero as opposed to atmospheric pressure, usually expressed as kPa, mm Hg or psia.

8.4. Cryogen - A refrigerant used to obtain very low temperatures for sample concentration. A typical cryogen is liquid nitrogen (bp - 195.8°C).

8.5. Dynamic calibration - Calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system in a manner very similar to the normal sampling or analytical process.

8.6. Gauge pressure - Pressure measured above ambient atmospheric pressure as opposed to absolute pressure. Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

8.7. MS-SCAN - The GC is coupled to a MS programmed in the SCAN mode to scan all ions repeatedly during the GC run. As used in the current context, this procedure serves as a qualitative identification and characterization of the sample.

8.8. MS-SIM - The GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly.

8.9. Qualitative accuracy - The ability of an analytical system to correctly identify compounds.

8.10. Quantitative accuracy - The ability of an analytical system to correctly measure the concentration of an identified compound.

9. EQUIPMENT AND SUPPLIES (INCLUDING COMPUTER HARDWARE AND SOFTWARE)

9.1. Equipment and Supplies Table

Supply	Description	Vendor/ Item # /
Gas Tight Syringes	0.010, 0.025, 0.05, 0.1, 0.25, 0.5, 1, 5, and 10 mL	Fisher, or equivalent
Neat liquid standards	at least 95%	O2Si, or equivilant
Glass static dilution flask	2L, equipped with a Mini-inert cap	Fisher, or equivalent
Oven	capable of maintaining a temperature of 65°C	Fisher, or equivalent
Summa ® passivated canisters or Silco ® lined canisters (or equivalent)	6L or 15L capacity	Restek
Dual pressure/vacuum gauge	high accuracy	Omega Engineering, or equivalent
Nitrogen		Praxair
Organic free water	DI Water	n/a
Gas Chromatograph	Equipped with a split/splitless injection port and electronic pressure control (EPC) or equivalent. See 9.1.1 and 9.1.2 for operating parameters.	Agilent Technologies 6890N
Mass Selective Detector	With Chemstation operating software and WinTarget data processing software or equivalent. See 9.1.3 for operating parameters.	Hewlett Packard 5973

Pre-concentrator	With 7016 canister manifold autosampler. See 9.1.4 for operating parameters.	Entech 7100A
Capillary Column	DB-5 60m x 0.32mm capillary column or DB-624 60m x 0.32mm with a 1.8 μm film thickness or equivalent.	J & W Scientific
Helium Cylinder	High purity grade high-pressure helium cylinder for column carrier gas equipped with a dual stage pressure regulator.	Praxair
Chemstation	Data Acquisition Software	See master list for current version
Target	Data Processing Software	See master list for current version
EPIC Horizon	Data Reporting Software (LIMS)	See master list for current version
Gandalph	Data Packaging Software	See master list for current version

9.1.1. Chromatograph Suggested Operating Parameters:

9.1.1.1. Initial temp: 40°C for 2.0 min.

9.1.1.2. Ramp A: 8°C/min to 150°C

9.1.1.3. Ramp B: 15°C/min to 200°C

9.1.1.4. Hold 2 min

9.1.1.5. EPC Pressure: 9 psi

9.1.1.6. Temp 250°C

9.1.1.7. Split Flow 20mL/min

9.1.2. Injection port parameters:

9.1.2.1. EPC pressure: 9 psi

9.1.2.2. Temperature: 250°C

9.1.2.3. Purge valve: Initial value On, Off time 0.0 min.

9.1.2.4. Split flow: 20 mL/min.

9.1.3. Suggested Mass spectrometer parameters:

9.1.3.1. Electron volts: 70 nominal

9.1.3.2. Scan range: 29 to 300 amu

9.1.3.3. Scan time: At least 2 scans/peak, not to exceed 1 sec/scan

9.1.3.4. Interface temp: 250°C

9.1.3.5. The GC/MS system must be set up to meet manufacturer's specification. The mass calibration and resolution of the GC/MS are verified by the analysis of the tune standard, p-bromofluorobenzene (BFB). For more information refer to the Chemsystem User's Guide and the GC/MS User's Guide.

9.1.4. Entech Pre-Concentrator suggested settings:

9.1.4.1.

During Concentration	Temperature (°C)
Module No. 1, Glass Bead Cryotrap	-150
Module No. 2, Sorbent Packed Cryotrap	-20
Focusing Trap	-160

9.1.4.2.

Desorb/Transfer/Inject	Preheat (ºC)	Final Temp(ºC)
Module No. 1, Glass Bead Cryotrap	10	10
Module No. 2, Sorbent Packed Cryotrap	50	180
Focusing Trap	N/A	N/A

9.1.4.3.

Media Concentrated/Transferred	Volume (cc)	Flow Rate (sccm)
Internal Standard & Surrogate	50	200
Sample	25 to 500	250
Sweep/Dry Purge	75	100
Transfer to Packed Column	40	10

9.1.4.4. Sample Transfer

Line Conditioning Sample Flush Before Trapping	20 sec
Carrier Flush Before Trapping	2 to 4 min.
Sample Transfer to Focusing Trap	2 to 4 min.
Sample Injection	2 to 5 min.

9.1.4.5.

System Bakeout	Temperature (ºC)	Time (min.)
Module No. 1	150	10
Module No. 2	190	10

9.1.4.6.

Regulated Zones	Temperature (ºC)
8-Port Valve	100
GC Transfer Line	110
Manifold Transfer Line	100
16-Position Select Valve	100
Sample Container	Ambient

10. REAGENTS AND STANDARDS

10.1. Target analyte standards are obtained from various vendors and verified for accuracy.

10.1.1. Calibration Mix is used for Initial Calibration (ICAL), Continuous Calibration (CCV) and Laboratory Control Spike (LCS). Second Source is used for initial calibration verification. Surrogate, Tuning and Internal standard solutions are obtained from vendors in solution form. These solutions are stored per manufacturer's specifications, and have an expiration date of one year after being opened or the manufacturer's expiration date if that date is prior to the one year date.

10.2. Reagents and Standards Table

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Calibration Standard	This is a custom mix that includes all compounds of interest at 1-5ppmv.	The calibration standard is purchased in the form of a pressurized cylinder from a source independent of the second source verification mix (Spectra Gas, Linde, Custom Gas Solutions, or equivalent).

Initial Calibration Verification (second source standard)	This is a custom mix that includes all compounds of interest at 1ppmv.	The ICV is purchased in the form of a pressurized cylinder from a source independent of the calibration mix.
Internal Standard/ Surrogate/ BFB Standard	Neat standards per each individual component.	The internal, surrogate, and BFB standards are purchased as separate neat standards from specific vendors; such as Chem-Service, Sigma-Aldrich or equivalent. See Attachment VI on preparation of working standard.

10.3. Working Standard Dilutions and Concentrations

10.3.1. All standards prepared into canisters in the air lab will be assigned a 28 day holding time, similar to the air samples. Upon expiration, the expired standard is removed from use and a new standard must be prepared.

Standard	Standard(s) Amount	Concentration of Std	Solvent	Solvent Volume	Final Total Volume	Final Concentration
2 PPBV Calibration Standard	90cc	1-5ppmv	Nitrogen	15 L Can	30psig	2-10 ppbv
20 PPBV Calibration Standard	900cc	1-5 ppmv	Nitrogen	15 L Can	30 psig	20-100 ppbv
Initial Calibration Verification Standard (ICV) (Second Source)	900 cc	1ppmv	Nitrogen	15L Can	30psig	20 ppbv
Method Blank	value less than RL	na	Nitrogen	500cc	500cc	less than RL
LCS	250cc	20ppbv	na	na	250cc	10-50ppbv

Ical Level	Concentration	Calibration Standard Used	Amt of Cal Standard Used
Level 1	0.10-0.50 ppbv	2.0-10.0 ppbv std	25 cc
Level 2	0.20-1.0 ppbv	2.0-10.0 ppbv std	50 cc
Level 3	0.50-2.5 ppbv	2.00-10.0 ppbv std	125 cc
Level 4	1.00-2.5 ppbv	2.00-10.0 ppbv std	250 cc
Level 5	10.00-50.0 ppbv	20.00-150.0 ppbv std	250 cc
Level 6	20.00-100.0 ppbv	20.00-150.0 ppbv std	500 cc
Level 7	30.00-150.0 ppbv	20.00-150.0 ppbv std	750 cc

10.3.2. Calibration Standard 2-10 PPBV: Using the 1000cc gas tight syringe, pull 90cc from TO15 Stock Standard Cylinder into a clean, evacuated 15L canister, that has been humidified with 50ul H2O. Pressurize the canister to 30 psig with clean nitrogen. This yields a final concentration of 2 ppbv. Record the standard ID, date created, analyst initial, canister number, canister volume, stock standard ID, volume used, water volume added, final pressure (psig), final concentration, and expiration date in the Pace Standard Preparation Logbook.

10.3.3. Calibration Standard 20-150 PPBV: Using the 1000cc gas tight syringe, pull 900cc from TO15 Stock Standard Cylinder into a clean, evacuated 15L canister, that has been humidified with 50 µL H2O. Pressurize the canister to 30 psig with clean nitrogen. This yields a final concentration of 20 ppbv. Record the standard ID, date created, analyst initial, canister number, canister volume, stock standard ID, volume used, water volume added, final pressure (psig), final concentration, and expiration date in the Pace Standard Preparation Logbook.

10.3.4. ICV 20 PPBV: Using the 1000cc gas tight syringe, pull 900cc from TO15 Stock Standard Cylinder into a clean, evacuated 15L canister, that has been humidified with 50ul H2O. Pressurize the canister to 30 psig with clean nitrogen. This yields a final concentration of 20 ppbv. Record the standard ID, date created, analyst initial, canister number, canister volume,

stock standard ID, volume used, water volume added, final pressure (psig), final concentration, and expiration date in the Pace Standard Preparation Logbook.

10.3.5. The ICV (Second Source Standard) is analyzed by injecting 250cc from the 20 ppbv ICV/Second Source standard (see above table)

10.3.6. To prepare Internal Standard/Surrogate/BFB:

Hexane D4	239ul
Toluene D8	195ul
Chlorobenzene D5	186ul
1,4 Difluorobenzene	179ul
BFB	201ul
1,4 Dichlorobenzne D4	0.277g

10.3.7. Example:

Barometric Pressure: 29.92

Room Temperature : 24 °C
Flask Temperature : 65 °C
Flask Volume : 2000 mL
Canister Pressure : 30 psig
Canister Volume : 15,000 mL (15 L)
Flask Concentration : 520.015 PPM

The procedure for Internal Standard/Surrogate/BFB standard is outlined in Attachment VI.

10.3.8. Next, pressurize the 15 L canister 30 psig with clean nitrogen. This yields a final concentration of 200 ppbv. Record the standard ID, date created, analyst initial, canister number, canister volume, stock standard ID, volume used, water volume added, final pressure (psig), final concentration, and expiration date in the Pace Standard Preparation Logbook. For each analysis, 25 cc is added during the trapping.

10.3.9. The tune standard, Bromofluorobenzene (BFB), must be 50ng or less on column.

10.3.9.1. The tune standard can be evaluated from thethe continuing calibration verification (CCV) standard so long as all criteria can be evaluated and met, since the BFB is present in all injections.

10.3.10. Internal standard compounds and surrogate standard compounds are used in the analysis.

10.3.10.1. Internal Standards: 1,4-Difluorobenzene and Chlorobenzene-d5

10.3.10.2. Surrogates*: Hexane-d14, Toluene-d8, and 1,2-Dichlorobenzene-d

*Surrogates are not a method requirement and therefore only reported at specific request of the client. Surrogates are not evaluated for Ohio VAP samples.

10.4. Standard Canister Preparation:

10.4.1. Static Dilution Technique

10.4.1.1. Summary: Standard preparation is accomplished by injecting an aliquot of liquid standard cocktail into a static dilution vessel (see 10.3.6). The static dilution vessel is held at a temperature of 55-75^{o}C. The liquid standard vaporizes and is quickly vented to come to equilibrium. An aliquot is removed and injected into a canister. The canister is then pressurized with nitrogen to a pre-established final pressure.

10.4.1.2. Procedure

10.4.1.2.1. The volume of a clean 2L round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density of 1 g/mL for water, the weight of the flask in grams when filled with water is taken as the volume of the flask in milliliters.

10.4.1.2.2. The dried flask is flushed with nitrogen. After a few minutes, the glass neck is immediately capped with a Mininert septum cap.

10.4.1.2.3. Predetermined aliquots of liquid standards are injected into the flask.

10.4.1.2.4. The flask is placed in the oven and allowed to equilibrate at a temperature sufficient to volatilize the liquid standard for about 30 minutes (55-75-°C). After 30 minutes, the flask is removed from the oven and allowed to cool to room temperature. .

10.4.1.2.5. Sample aliquots are then to be taken from the static dilution flask for introduction into a clean, evacuated canister. The canister is then filled to a final predetermined pressure. An aliquot or aliquots totaling greater than 1 percent of the flask volume are to be avoided.

10.4.1.2.6. The concentration of each component in the flask is calculated using Equation 1 (see section 14).

10.4.1.2.7. The concentration in ppbv of each component in the flask is determined using Equations 2 and 3 (see section 14).

10.4.1.2.8. The concentration in ppbv of each compound in the canister can be determined using Equation 4 (see section 14).

10.4.1.2.9. Entech Standards Preparation has a database of compounds and their properties. The program does the necessary conversions of units and calculations (equations 1-4) to yield the amounts of neat standard put in the standard cocktail, the amount of cocktail spiked into the 2L flask, and the aliquot taken from the 2L flask to the final canister. This program can be used to make any gas standard from neat liquid standards.

10.4.1.2.10. See Attachment VI for a single sheet summary of Air Standard Preparation.

11. CALIBRATION AND STANDARDIZATION

11.1. Calibration CriteriaTable

Calibration Metric	Parameter / Frequency	Criteria	Comments
Instrument Tune	Before any standard, method blank, or sample analysis can occur using the GC/MS system, it must be demonstrated that the GC/MS is capable of producing compliant spectra when p-bromofluorobenzene (BFB) is analyzed. Attachment II lists the required spectral criteria. The instrument performance check must be analyzed initially and once every 24-hour period. The tune period begins at the time of injection of the BFB.	If the BFB spectrum meets the criteria listed in Attachment II, proceed with standard and sample analysis. If the BFB spectrum fails to meet the criteria listed in Attachment II, the MS must be retuned. Repeated failures potentially indicate the need for MS maintenance such as cleaning the ion source.	The GC/MS is set up according to the manufacturer's specifications. The MS source and mass filter are adjusted by monitoring the mass spectra of Perfluorotributylamine (PFTBA). Prepare a standard solution of BFB at a concentration that allows the collection of 50ng or less under the optimized concentration parameters (see Section 10.3). This is met by injecting 25 cc during the trapping. The BFB is introduced into the system through microscale purge and trap. The spectrum of BFB must be acquired by averaging three scans; the apex and the scans that immediately proceed and follow the apex. Background subtraction is

			accomplished using a single scan taken before the BFB peak.
Initial Calibration (ICAL)	Initial Calibration is performed as a result of extensive instrument maintenance, multiple CCV outliers for analytes of interest, Internal Standard Non Compliance, and at the discretion of the analyst. All standards, method blanks, laboratory control spikes (LCS), and samples must be analyzed using the same conditions. A calibration curve must consist of a minimum of 5 standards (6 for quadratic) and spans the expected monitoring range established for each compound of interest to determine instrument response and linearity. The lowest level of the curve must be at or below the reporting limit for each analyte. A typical calibration curve can cover a range from 0.1 to 20 ppbv. Section 10.3 contains standard preparation information.	The %RSD for all calibrated target compounds must be ±30%. Alternately for all target compounds, linear regression is used with an r^2 value of 0.995 or greater. A quadratic curve is utilized if the r^2 (equals COD in Equation 12) value is 0.990 or greater and six calibration points are included in the curve. Curves must not be forced through zero. *For Ohio VAP: quadratic curve fit is only to be used for analytes that have historically exhibited nonlinear response.* The area response for each internal standard in each calibration level must be within 40% of the mean area response over the calibration range. The relative retention time (RRT) of each compound must agree within ± 0.06 RRT units of the average RRT from the initial calibration curve. Per the Pace Quality Assurance Manual, the reporting limit standard must be evaluated to determine if the curve fit is presenting bias. The level corresponding to the reporting limit must be quantitate back after processing the curve and be ± 40% of the expected true value. See section 11.2 for corrective actions.	Initial calibrations are not meant to be a replacement of necessary instrument maintenance. Calibration curve fits are possible indicators of instrument performance or deterioration. Analytes that traditionally are average or linear responders that suddenly display quadratic curve fits could be a sign of a system that is deteriorating. Quadratic cannot be used to extend the calibration range for compounds that normally exhibit a linear response, perform necessary maintenance to return the system to good working order. This is not to eliminate the use of quadratic curve fits, some analytes always present a quadratic response and that is acceptable. If an analyte fails to meet ICAL criteria, the analyst should report sub list of compounds and/or re-analyze samples under compliant conditions. Calibration is performed using the internal standard technique. See Attachment III for internal standard groups. The data is evaluated using WinTarget. See section 11.2 for acceptance criteria.
Initial Calibration Verification (ICV)	A second source standard must be analyzed following an initial calibration curve which contains all the analytes of interest.	The spike level of the ICV must be near the midpoint level of the calibration curve. The ICV is considered acceptable if the recoveries of the analytes fall within 60-140%. •	The ENTECH 7000 Concentrator automatically adds 25 cc of the internal standards and surrogates (Section 10.3) to each analysis during trapping. Using the Target data processing software, evaluate the calibration data.
Continuing Calibration Verification (CCV)	After an acceptable tune has been evaluated, the initial calibration curve for each compound of interest must be checked and verified before sample	The %D for each target compound in the continuing calibration verification (CCV) standard must be less than or equal to 30 percent. The RRT of each compound must	Calculate the RRF for each target compound from the continuing calibration standard using Equation 5 (see section 14). See 11,3 for corrective action.

	analysis can occur each day. This is accomplished by analyzing continuing calibration verification (CCV) standard at 10 ppbv (see section 10.3 Ical Level 5). The CCV is the same source as the ICAL standard. The CCV is analyzed after a compliant tune once every 24-hour period during sample analysis.	agree within ± 0.06 RRT units of the average RRT from the initial calibration curve. See 11.3 for corrective actions.	Note: If a CCV fails biased high and the associated samples are non-detect, the samples may be reported as the high bias has no impact on the non-detect results.

11.2. Corrective Action for Initial Calibration

11.2.1. If ICV fails criteria, the analyst must consult with his or her supervisor or manager before moving forward. Possible corrective actions include:

11.2.1.1. The system and standards must be evaluated for potential problems. If a problem is isolated and corrected, attempt to run a second ICV. If the second attempt also does not meet criteria, perform further necessary troubleshooting and maintenance.

11.2.1.2. Check pressure on the standard canister.

11.2.1.3. Check system for leaks.

11.2.1.4. Check to see that standards were made correctly.

11.2.2. If the ICV was injected during a period in which it could not be evaluated immediately and was followed by a SDG, data impact is evaluated and reported with necessary footnotes pending supervisor or manager approval.

11.2.3. If the technical acceptance criteria fail for the initial calibration curve, inspect the system for any possible leaks. A high baseline and reduced response potentially indicates a leak.

11.2.4. Examine the response factors of each calibration level. If the response factors of all the compounds for one level appear to be significantly different, analyze that same level calibration standard again.

11.2.5. If the same results occur after reanalysis, a new standard canister must be made and analyzed.

11.2.6. If a leak or other system problem cannot be found, try to clean the ion source or perform column maintenance.

11.2.7. No samples can be analyzed until a compliant initial calibration curve has been established and verified against a second source standard or technical justification has been given for analysis to proceed. Technical justification would be if there are samples available that require only a short list of analytes that exclude the failures, analysis may continue for those analytes. Clearly document which elements are not acceptable on the analytical checklist. If sample analysis has occurred prior to the ICAL being evaluated, samples that are unable to be reanalyzed may have to be reported. The client must be contacted and the data results must be clearly qualified indicating the associated ICAL failures.

11.2.8. Recalibration must be performed if any major change has been made to the GC/MS system such as replacing the GC column, cleaning the MS source or repair.

11.3. Corrective Action for Continuing Calibration Verification

11.3.1. If the CCV does not meet criteria, the system and standards must be evaluated for potential problems. If a problem is isolated and corrected, attempt to run a second CCV. If the second attempt also does not meet criteria, perform further necessary troubleshooting and maintenance.

11.3.1.1. Check pressure on the standard canister.

11.3.1.2. Check system for leaks.

11.3.1.3. Check to see that standards were made correctly.

11.3.1.4. Document all maintenance and corrective action measures taken in the maintenance logbook, run logbook or checklist accordingly based on the actions taken.

11.3.2. If corrective action attempts fail or two consecutive CCV do not meet criteria, then a new calibration curve must be analyzed.

11.3.3. Samples are not to be analyzed until CCV criteria has been met or technical justification as defined in 11.2.5 has been given for the analysis to continue.

12. PROCEDURE

12.1. Analytical Sequence

12.1.1. The following is the GC/MS analytical sequence for samples each 24-hour period:

12.1.1.1. CCV, which also serves as the Laboratory Control Standard for the batch of twenty samples. Two CCVs are permitted to be analyzed on each system before an Initial Calibration is needed.

In the event the CCV is not compliant for analytes of interest in the samples, and Initial Calibration is required before sample analysis. An ICAL is followed then by the ICV. The ICV may be used as the Laboratory Control Standard or LCS.

12.1.2. Laboratory Method Blank: 500cc of nitrogen from a clean 6L canister.

12.1.2.1. 20 field samples

12.1.2.2. Sample duplicate, minimum of one in 20 samples

12.1.2.3. Any necessary dilutions from previously analyzed samples (see the dilution preparation section of Attachment V).

12.1.2.4. In the event that time remains in the 24 hour tune period, an additional method blank and LCS must be analyzed in order to analyze additional reportable samples.

12.2. Sample Analysis

12.2.1. Upon receipt, the canister pressure of each sample is measured and recorded on the canister sample tag.

12.2.1.1. If the canister pressure is less than 5 psig, the canister pressure must be increased before analysis can occur.

12.2.1.1.1. Add clean nitrogen or helium gas to the sample canister. For a six liter canister, 5 psig is the desired final pressure. A one liter canister requires a final pressure of 10 psig for adequate sample volume for analysis.

12.2.1.1.2. Record the final canister pressure on the canister sample tag noting which gas was added. Also, note the information in the final analytical results report.

12.2.1.1.3. Calculate the resultant dilution factor using Equation 16 in section 14.16.

12.2.1.1.4. This dilution factor is applied to Equation 17 in section 14.17.

12.2.2. Once the GC/MS system is demonstrated to be in control, an aliquot of the air sample is removed from the canister and pre-concentrated using the Entech 7100A pre-concentrator and 7016 autosampler manifold.

12.2.3. Analyze the samples under the same operating conditions as the instrument calibration and quality control samples.

12.2.4. Analyze a duplicate sample for every 20 samples analyzed.

12.2.5. If time remains in the 24-hour tune period in which an initial calibration was performed, it is possible to continue to analyze samples without the analysis of a CCV standard.

12.2.6. If the tune period has expired, an instrument tune and CCV standard must be analyzed before samples can be analyzed.

12.2.7. If time remains in the tune period after a batch of no more than 20 samples and its re-runs have been analyzed, it is possible to analyze additional samples after a new LCS and method blank have been analyzed.

12.2.8. Technical Acceptance Criteria can be found in Section 12.7.

12.2.9. Procedures for the determination of Air Phase Petroleum Hydrocarbons (APH) can be found on Attachment XII. Reporting of APH can only be conducted per each state or client acceptance of the data, i.e. Ohio VAP only allows the analysis of the TO15 analytes listed in Table 1 and as specified the Pace scope of accreditation. See the most current certificates for the approved analyte lists, any analytes not approved must be clearly indicated on the report and affidavits as being compounds not certified by the VAP program.

12.3. Qualitative Analysis

12.3.1. The compounds listed in Attachment I are identified by an analyst competent in the interpretation of mass spectra. Sample mass spectrum is compared to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the target compound identifications: (1) elution of the sample component at the same GC retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

12.3.2. The relative retention time (RRT) of the sample component must agree within ± 0.06 RRT units of the RRT of the standard component using the CCV standard as reference.

12.3.3. Standard and sample mass spectra are compared using reference spectra obtained on the GC/MS system being used. The mass spectra used for comparison are from the same standard as that being used for RRT comparison. Mass spectral requirements are as follows:

12.3.3.1. 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.

12.3.3.2. The relative intensities of ions specified above must agree within ± 20% between the standard and sample spectra.

12.3.3.3. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process favors false positive.

12.3.4. Non-target sample components are library searched using the latest NIST library for the purpose of tentative identification. These components are referred to as TICs - Tentatively Identified Compounds) and are noted as such in any final report with a qualifier of "J" unless the client specifies differently. The "J" qualifier indicates an estimated value. Guidelines for identification are as follows:

12.3.4.1. Characteristic ions in the reference spectrum (ions greater than 10% of the most abundant ion) must be present in the sample.

12.3.4.2. The relative intensities of the major ions must agree within ± 20%.

12.3.4.3. Ions present in the sample spectrum but not in the reference spectrum must be reviewed for background contamination or presence of co-eluting peaks.

12.3.4.4. If in the technical judgment of the analyst, no valid identification can be made, the compound is to be reported as an unknown with possible classification, such as hydrocarbon.

12.3.4.5. TIC searches are reported only upon client request. These results are considered estimated and do not fall under any scope of accreditation held by Pace.

12.4. Identified target analytes are quantitated using the internal standard method using the extracted ion current profile (EICP) area of the characteristic ions of analytes listed in Attachment III. This ion is referred to as the quantitation ion.

12.5. The RRF from the initial calibration curve analysis is used to quantitate samples and method blanks. Calculate the concentration of the sample component using Equation 17 in section 14.17.

12.5.1. Additional curve fit equations are in section 14.

12.6. The internal standard method of quantitation is also used to determine an estimated concentration for Tentatively Identified Compounds (TIC). The nearest internal standard to the TIC is used as a reference to estimate the concentration of the TIC. If the nearest internal standard exhibits interferences, the next closest internal is used. The estimated concentration is obtained using Equation 17 with the following exceptions:

A_x =Total ion chromatogram area of the TIC,
A_i =Total ion chromatogram area of the specific internal standard;
R_f =1.0

Estimated TIC concentrations are flagged with a qualifier of "J" which indicates that the quantitated amount is an estimate. TICs are not considered certified analytes under any scope of accreditation. If TICs are reported, they must be clearly indicated as not being certified analytes under the program that the work is related to.

12.7. General Technical Acceptance Criteria

12.7.1. For data to be reported without qualification, the following criteria must be met for all samples, CCVs, method blanks, and laboratory control sample (LCS).

12.7.1.1. The EICP area response for each internal standard must be within ±40% of the EICP area response in the most recent CCV. See Attachment III for a list of analytes and assigned internal standards.

12.7.1.2. The retention time for each of the internal standards must be ±0.33 minutes of each of the internal standard (IS) retention times in the most recent ICAL 10.0 Standard.

12.7.1.3. Recoveries for surrogate standard compounds (where required) must fall within ±30% of the true value.

12.7.2. If the technical acceptance criteria are not met, samples must be reanalyzed with appropriate batch QC to confirm results under compliant operating conditions. This confirmation is performed by reanalyzing the corresponding QC that was out of range with the samples and if found to be not in range, narrative for bias will be noted, as applicable. See Section 11.2 and 11.3 for corrective action for calibration failures and Section 13.1 for all other samples (including QC).

12.7.3. There will be times in which analytical results are obtained outside the linear range due to highly contaminated sites. Pace makes every attempt to dilute the samples within the linear range of the instrument. If sufficient dilutions cannot be made to achieve results within the linear range because of sample size or concentration, the data will be reported qualified as estimated. If the bias can be noted, it will be qualified accordingly in the final report, i.e. biased high or biased low.

13. QUALITY CONTROL

13.1. QC Table

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	A clean canister filled with humidified nitrogen is analyzed on the GC/MS system to demonstrate that the	Analyzed once every 24-hour period or every 20 samples, whichever	An instrument blank analysis is allowed after any sample that has known VOCs present that exceed the	Re-analyze associated samples. ***Exceptions:*** If sample ND, report sample without qualification;

	system is free of interferences. The Method Blank is prepared in the same manner as any standard or sample and analyzed in the same manner.	comes first. The Method Blank is analyzed before samples can be analyzed, and after daily ICAL or CCV.	upper calibration limit of the method to demonstrate that the system is free of possible carryover effects. When possible, historical data can be used to determine if there are high levels of contaminants present, possibly causing carry over in the system. The method blank must not contain any target analyte at a concentration greater than its reporting limit and must not contain additional compounds with elution characteristics and mass spectral features that interfere with identification and measurement of a method analyte. The internal standard must be within ± 40% of the mean area response of the IS in the most recent calibration. The retention time of each of the internal standards must be within ± 0.33 minutes between the method blank and the most recent calibration standard.	If sample result >10x MB detects, report the data as it is not impacted by the blank detections; If sample result <10x MB detects and cannot be reprepared/reanalyzed, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition. NOTE: For Ohio VAP samples, if the detection is above the reporting limit and corrective actions as listed in this table do not result in acceptable data, the samples must be re-analyzed If re-analysis is not possible due to depleted sample volume, then contact the client for further instructions. The client can choose to re-submit the sample or have the lab qualify the data and narrate as appropriate. The narrative for any report that includes qualified data must also include a discussion of any bias in the results.
Laboratory Control Sample (LCS)	The laboratory control standard is prepared from the same standard as the calibration standard) as outlined in section 10.3. The LCS standard is from the same source as the ICAL standard.	A LCS must be analyzed once every 24-hour period or every 20 samples, whichever is more frequent.	The percent recovery for each analyte in the LCS must be within the internally generated recovery limits and can be found in the LIMS system.	If a LCS fails to meet the recovery limit criteria, inspect the system for the possibility of a poor sampling. If the LCS fails and no error in sampling was found, preparation and injection of a second analysis can be conducted. If that second analysis fails, the system must be recalibrated and all affected samples must be reanalyzed. If the samples cannot be

				reanalyzed, qualify the data accordingly with an appropriate footnote on the final report indicating the bias present. For Ohio VAP samples, if the outlier is an analyte of interest and corrective actions as listed in this table do not result in acceptable data, the QC and samples must be re-analyzed. If re-analysis is not possible due to depleted sample volume, then contact the client for further instructions. The client can choose to re-submit the sample or have the lab qualify the data and narrate as appropriate. The narrative for any report that includes qualified data must also include a discussion of any bias in the results.
Duplicate Samples	Client provided samples.	Duplicate sample analysis is performed once per 20 samples	The RPD between the sample and the sample duplicate must be < 25%.	If the RPD fails to meet criteria, the instrument must be evaluated to determine if there was an error with the analysis. If there is not evidence of malfunction, the parent sample must be reanalyzed to confirm results. If the data confirms, report the original data and qualify the bias accordingly. Contact the client for further instructions. The client can choose to re-submit the sample or have the lab qualify the data and narrate as appropriate. The narrative for any report that includes qualified data must also include a discussion of any bias in the results.
Internal Standards	Internal standard is added to every injection at a concentration of 10ppbv.	Aliquot is added to each analysis at the pre-concentrator.	The EICP area response for each internal standard must be within ±40% of the EICP area response in the mid point of the initial calibration. See Attachment III for a list of analytes and assigned internal standards.	Examine the instrument for possible errors or malfunctions and correct any that are discovered. Re-analyze the samples and associated batch QC samples:method blanks, laboratory control spike, and sample duplicates). Report the reanalyzed sample results accordingly. If there is no evidence of error or malfunction, re-analyze the affected QC and samples. If the data confirms, report the original data and qualify the bias accordingly.

				Unless a matrix interference was detected, Ohio VAP samples must be re-analyzed undiluted. If the outlier corrective actions do not result in acceptable data, the samples must be re-analyzed. The narrative for any report that includes qualified data must also include a discussion of any bias in the results.
Surrogate	Labeled compounds that behave similarly to target analytes that are meant to represent the efficiency of the system related to the matrix	Included in each injection per client specific QAPPs. Surrogates will not be injected into any samples or standard/QC solutions for analysis intended for Ohio VAP certified data.	Internally generated control limits. Most current limits are found in the LIMS.	Confirm that there are no errors in the calculations, surrogate solutions, and internal standards. Verify instrument performance. If no problems are found, reprepare and reanalyze the sample. If the reanalysis is within limits and holding times, then report only the reanalysis. If the reanalysis is within limits, but out of hold, then report both sets of data. If the reanalysis is still out of limits, then report both sets of data.

14. DATA ANALYSIS AND CALCULATIONS

14.1. See the most current Quality Manual for calculations

14.2. Concentration of each component in the flask (Static Dilution Technique, section 10.4.1)

Equation 1

$$\text{Concentration}(\text{mg/L}) = \frac{(V_i)(d)}{V_f}$$

where:

V_i =Volume of liquid neat standard injected into the flask in mL;
d=Density of the liquid neat standard in mg/mL;
V_f =Volume of the flask in liters.

Caution: In the preparation of standards by this technique, make sure that the volume of neat standard injected into the flask does not result in an overpressure due to the higher partial pressure produced by the standard compared to the vapor pressure in the flask.

14.3. The concentration in ppbv of each component in the flask is determined using Equations 2 and 3 (Static Dilution Technique, section 10.4.1)

14.3.1. First determine the volume of the compound as a gas using Equation 2:

Equation 2

$$V = \frac{nRT}{P} \quad \text{where,} \quad n = \frac{(V_i)(d)}{M}$$

where,
V=Volume of injected compound at STP in liters;
n=Moles;
R=Gas constant (0.08206 L-atm/mole ^{o}K);
T=Ambient temperature in ^{o}K;
P=Ambient pressure in atm;
V_i=Volume of liquid neat standard injected into the flask in mL;
d=Density of the neat standard in g/mL;
M=Molecular weight of the compound in g/mole.

14.3.2. Now calculate the concentration in the flask in ppbv using Equation 3:

Equation 3

$$\text{ppbv} = \frac{V}{V_f}\left(10^9\right)$$

where:
V=Gas volume of compound as determined in Eq. 8 in liters;
V_f=Volume of static dilution flask in liters.

14.4. The concentration in ppbv of each compound in the canister can be determined using Equation 4 (Static Dilution Technique, section 10.4.1)

Equation 4

$$\text{ppbv} = \frac{(V_i)(C_x)}{V_c}$$

where:
V_i=Volume removed from static dilution flask and injected into the canister in liters;
C_x=Concentration of compound x in the static dilution flask in ppbv;
V_c=Final canister volume in liters.

14.5. Relative Response Factor (RRF): Tabulate the area response of the primary ion (Attachment III) for each compound and the associated internal standard. Use the internal standard, which has a retention time nearest to the compound of interest. Calculate the relative response factors (RRF) for each compound using Equation 5:

Equation 5

$$\text{Relative Response Factor (RRF)} = \frac{(A_x)(C_i)}{(A_i)(C_x)}$$

where,
A_x=Area of the primary ion for compound x to be measured;
A_i=Area of the primary ion for the internal standard associated with compound x;
C_i=Concentration of the internal standard in ppbv;
C_x =Concentration of compound x to be measured in ppbv.

14.6. Mean Relative Response Factor. Calculate the mean RRF for each compound using the RRF from the five (or six, where n=6)-point calibration using Equation 6:

Equation 6

$$\overline{R_f} = \frac{\sum_{n=5} R_f}{n}$$

where,

$\overline{R_f}$ =Average relative response factor;

R_f=Relative response factor from calibration curve;

n=Number of data points.

14.7. Standard Deviation ($\sigma_{(n-1)}$).

Equation 7

$$\sigma_{(n-1)} = \sqrt{\sum_{i-1}^{n} \frac{(x_i - \bar{x})^2}{(n-1)}}$$

14.8. %Relative Standard Deviation (%RSD). Using the average RRF from Equation 6 and the standard deviation from Equation 7, calculate the %RSD using Equation 8:

Equation 8

$$\%RSD = \frac{s_{(n-1)}}{\bar{R}_f} x100$$

14.9. Mean area response for Internal Standard:

Equation 9

$$\bar{y} = \sum_{i=1}^{n} \frac{y_i}{n}$$

where,

$\bar{y}$ = mean area response

y = Area response for the internal standard for each initial calibration standard

14.10. If a linear regression is used, the regression produces the slope and intercept terms for a linear equation according to Equation 10:

Equation 10

$y = ax + b$

where:

y = instrument response (peak area or height)

a = Slope of the line (also called the coefficient of x)

x = Concentration of the calibration standard

b = the intercept, do not include the origin (0) as a calibration point

14.11. To calculate the sample concentration by the internal standard method using the linear regression equation, use Equation 11:

Equation 11

$C_s=[(A_sC_{is}/A_{is})-b]/a$

where:

As = Area of the peak for the target analyte in the sample

Ais = Area of the peak of the internal standard
Cs = Concentration of the target analyte in the calibration standard
Cis = Concentration of the internal standard
a = Slope of the line (also called the coefficient of Cs)
b = The intercept

14.12. To calculate the coefficient of determination (or r^2) for a quadratic curve fit, use Equation 12:

Equation 12

$$COD = \frac{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - Y_i)^2}{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2}$$

where:
y_{obs} = Observed response for each concentration from each initial calibration standard
y = Mean observed response from the initial calibration (See equation 6)
Y_i = Calculated response at each concentration from the initial calibration (See Equation 5)
n = Total number of calibration points in the equation, 6 points for quadratic
p = Number of adjustable parameters in the polynomial equation

14.13. Calculate the sample concentration by the internal standard method using the quadratic regression by comparing peak heights to the calibration curve.

Equation 13

Regression equation (quadratic):

$y = ax^2 + bx + c$

14.14. Percent Difference (%D). The % D in the RRF of the daily RRF of an individual compound compared to the mean RRF for that compound in the most recent calibration curve is determined as follows:

Equation 14

$$\%D = \frac{|R_i - R_c|}{R_i}(100)$$

where,

R_i=The average RRF from the initial calibration curve for compound *x*;
R_c=RRF for compound *x* from the CCV standard.

14.15. Calculate the percent recovery of the LCS using Equation 15:

Equation 15

$$\text{Percent Recovery} = \frac{C_q}{C_a}(100)$$

where:

C_q=Quantitated concentration of compound *x* in ppbv;
C_a=Actual concentration of compound *x* in ppbv.

14.16. Calculate the resultant dilution factor using Equation 16:

Equation 16

DF = (Pf + 14.7) / Pi + 14.7)

Pi = Pressure reading of canister prior to pressurization (psig)
Pf = Pressure reading of canister after pressurization (psig)
DF = Dilution factor

To convert Hg to psig:
Multiply by 0.491559 or divide by 2.036

PSIG reading is converted to One Atmosphere:
One Atmosphere = 14.7 psig = 29.21 inches of Hg

See Attachment V for the application of dilution factors for filling canisters.

14.17. Calculate the concentration of the sample component using Equation 17:

Equation 17

$$C_x = \frac{(A_x)(C_i)(D_f)}{(A_i)(R_f)}$$

where:

C_x=Concentration of compound *x* in ppbv;
A_x=EICP area of the quantitation ion for compound *x*;
C_i=Concentration of the internal standard associated with compound *x* in ppbv;
D_f=Dilution factor from Equation 12 (if no dilution was performed, D_f equals 1.)
A_i=EICP area of the quantitation ion for the internal standard associated with compound *x*;
R_f=Average RRF for compound *x* from the most recent calibration curve.

14.18. The RPD between the sample and the sample duplicate can be calculated using Equation 18:

Equation 18

$$RPD = \frac{|A-B|}{(A+B)/2} \times 100$$

Where:

RPD = Relative Percent Difference
A = Sample Value
B = Duplicate Value

14.19. Convert ppbv to µg/m^3 using Equation 19:

Equation 19

$$\frac{(x\,ppbv \times MW\frac{g}{mol})}{24.055\frac{L}{mol}} = y\frac{\mu g}{m^3}$$

Where:

MW = Molecular Weight
24.055 L/mol = Molar Volume of an ideal Gas

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

Where:

V = Volume in liters
N = mols of ideal Gas (1 mol)
R = Ideal gas constant
T = Temperatire in Kelvin

$$V = \frac{(1mol) \times (0.082 \frac{(L \times atm)}{(mol \times K)} \times 293.15K}{1\ atm}$$

$$V = 24.055 \frac{L}{mol}$$

14.20. Preparation of Working TO15 Standard can be calculated using equation 20:

Equation 20

$$\frac{X}{Y} \times C = Z$$

Where:

X = Volume (L) spiked from stock
Y = Volume (L) of container
C = Concentration (ppbv) of Stock
Z = Concentration (ppbv) of working standard

15. DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

15.1. See tables in section 11 & 13.

16. CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

16.1. See tables in section 11 & 13.

17. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

17.1. If not specifically listed in the tables in section 11 & 13, the contingencies are as follows. If there is no additional sample volume to perform re-analyses, all data will be reported as final with applicable qualifiers. If necessary, an official case narrative will be prepared by the Quality Manager or Project Manager.

17.2 Any data that is reported not meeting method specifications will be qualified accordingly using footnotes in the LIMS or custom qualifiers using the text field. These footnotes will be designated next to the analytes impacted with a letter/number combination with a summary of definition in the footnote section of the final report. Depending on the client data quality objective, an additional case narrative may be included in the final report and the qualifiers will be summarized in that section of the report as well. As indicated throughout the document, Ohio VAP requires the bias be included in the data qualification and associated case narrative.

18. METHOD PERFORMANCE

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. Three performance criteria are used to demonstrate method validity which are: (1) method detection limit (MDL), (2) replicate precision, and (3) accuracy - % recovery of LCS.

18.3. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually (per the method) per S-MN-Q-269 (or equivalent replacement), Method Detection Limit Studies for each matrix per instrument.

18.4. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) S-ALL-Q-020 (or equivalent replacement), Training Procedures.

18.5. **Periodic performance evaluation (PE)** samples are analyzed periodically to demonstrate continuing competence per SOP S-MN-Q-258 (or equivalent replacement). Results are stored in the Quality office.

19. METHOD MODIFICATIONS

19.1. Pace utilizes 1,4-Difluorobenzene and Chlorobenzene-d5 as internal standards. This is a modification from the three recommended internal standards in the method. Pace has demonstrated with MDLs, ICAL/ICV and PTs that this does not impact the data results.

19.2. Pace utilizes clean nitrogen for cleaning and filling canisters used for samples and standards. This is a modification from the method use of zero air.

19.3. Pace initial calibrations are accepted with average response models, as well as linear and quadratic regression models. Pace utilizes percent drift when analyzing continuing calibrations with regression models. Acceptance criteria utilized is the same as percent difference (±30% of the midpoint of the most recent ICAL). This process has been adapted from EPA method 8260B. Refer to section 25.8.

19.4. Pace utilizes a temperature range for the preparation of internal standards described in section 10.4.1.2. Final concentration is not dependent upon the temperature used to heat the round bottom flask and is only required to sufficiently volatilize any liquid standards in the vessel.

20. INSTRUMENT/EQUIPMENT MAINTENANCE

20.1. All maintenance activities are listed daily in maintenance logs that are assigned to each separate instrument.

20.2. Refer to the instrument user's manual for instrument maintenance.

21. TROUBLESHOOTING

21.1. Not applicable to this SOP.

22. SAFETY

22.1. Standards and Reagents: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. Samples: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

23. WASTE MANAGEMENT

23.1. Procedures for handling waste generated during this analysis are addressed in S-MN-S-003, Waste Handling, or equivalent replacement.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (e.g., before a reagent expires).

24. POLLUTION PREVENTION

24.1. The company wide Chemical Hygiene and Safety Manual contains information on pollution prevention.

25. REFERENCES

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. Department of Defense (DoD) Quality Systems Manual- most current version.

25.5. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition; USEPA, January 1999; EPA/625/R-96/010b. Compendium Method TO15.

25.6. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition; USEPA, January 1999; EPA/625/R-96/010b. Compendium Method TO14A MA DEP Air Phase Petroleum Hydrocarbon (APH) method, 12/2009.

25.7. Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). Section 7.4.5.

26. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

26.1. ATTACHMENT I: Target Compound List

26.2. ATTACHMENT II: Required BFB Key Ions and Ion Abundance Criteria

26.3. ATTACHMENT III: Characteristic Ions for Target Compounds

26.4. ATTACHMENT IV: Calibration of THC as Gas

26.5. ATTACHMENT V: Canister Dilution Factors

26.6. ATTACHMENT VI: Air Laboratory Standard Preparation Procedures

26.7. ATTACHMENT VII: Procedures for Analyzing MPCA Samples

26.8. ATTACHMENT VIII: Procedure for Tedlar Bags

26.9. ATTACHMENT IX: Tedlar Sign-off Logbook

26.10. ATTACHMENT X: Tedlar Bag Transfer Log

26.11. ATTACHMENT XI: Common Logbook Abbreviations

26.12. ATTACHMENT XII: Determination of Air Phase Petroleum Hydrocarbons (APH)

27. REVISIONS

Document Number	Reason for Change	Date
S-MN-A-013-Rev.20	Updated to LLC throughout document	19Dec2016

ATTACHMENT I - Target Compound List

Compound	CAS RN	TO14 compounds
1,1,1-Trichloroethane	71-55-6	X
1,1,2,2-Tetrachloroethane	79-34-5	X
1,1,2-trichloroethane	79-00-5	
1,1-Dichloroethane	75-34-3	X
1,1-Dichloroethene	75-35-4	X
1,2,4-Trichlorobenzene	95-63-6	X
1,2,4-Trimethylbenzene	95-63-6	X
1,2-Dibromoethane	106-93-4	X
1,2-Dichlorobenzene	95-50-1	X
1,2-Dichloroethane	107-06-2	X
1,2-Dichloropropane	78-87-5	X
1,3,5-Trimethylbenzene	108-67-8	X
1,3-Butadiene	106-99-0	
1,3-Dichlorobenzene	541-73-1	X
1,4-Dichlorobenzene	106-46-7	X
4-Ethyltoluene	622-96-8	
Acetone	67-64-1	
Acrolein	107-02-8	
Acrylonitrile	107-13-1	
Benzene	71-43-2	X
Benzyl Chloride	100-44-7	
Bromodichloromethane	75-27-4	
Bromoform	75-25-2	
Bromomethane	74-83-9	X
Carbon Disulfide	75-15-0	
Carbon Tetrachloride	56-23-5	X
Chlorobenzene	108-90-7	X
Chloroethane	75-00-3	X
Chloroform	67-66-3	X
Chloromethane	74-87-3	X
Cis-1,2-Dichloroethene	156-59-2	X
Cis-1,3-Dichloropropene	10061-01-5	X

ATTACHMENT I (continued) - Target Compound List

Compound	CAS RN	TO14 compounds
Cyclohexane	110-82-7	
Dibromochloromethane	124-48-1	
Dichlorodifluoromethane	75-71-8	X
Dichlorotetrafluoroethane	76-14-2	X
Ethanol	64-17-5	
Ethyl Acetate	141-78-6	
Ethyl Benzene	100-41-4	X
Freon 113	76-13-1	X
Heptane	142-82-5	
Hexachlorobutadiene	87-68-3	X
Hexane	110-54-3	
Isopropyl Alcohol	67-63-0	
M,P Xylene	106-42-3	X
O-Xylene	95-47-6	X
Methyl Butyl Ketone	591-78-6	
Methyl Ethyl Ketone	78-93-3	
Methyl Isobutyl Ketone	108-10-1	
Methyl Tert Butyl Ether	1634-04-4	
Methylene Chloride	75-0902	X
Napthalene	91-20-3	
Propylene	115-07-1	
Styrene	100-42-5	X
Tetrachloroethene	127-18-4	X
Tetrahydrofuran	109-99-9	
Toluene	108-88-3	X
Trans-1,2-Dichloroethene	156-60-5	
Trans-1,3-Dichloropropene	10061-02-6	X
Trichloroethene	79-01-6	X
Trichlorofluoromethane	75-69-4	X
Vinyl Acetate	108-05-4	
Vinyl Chloride	75-01-4	X

*Current reporting limits can be found in Horizon

Note*: *Any analytes not approved must be clearly indicated on the report with the affidavits as being compounds not certified by Ohio VAP program.

ATTACHMENT II - Required BFB Key Ions And Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95 (See note)
173	less than 2.0 percent of mass 174
174	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

Note: All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

ATTACHMENT III - Characteristic Ions For Target Compounds

Compound	Primary Ion	Secondary Ion(s)	Internal Standard Group
Propylene	41	39	1
Dichlorodifluoromethane	85	87	1
Chloromethane	50	52	1
Dichlorotetrafluoroethane	85	135,87	1
Vinyl Chloride	62	64	1
1,3-Butadiene	54	39	1
Bromomethane	94	96	1
Chloroethane	64	66	1
Ethanol	31	45	1
Trichlorofluoromethane	101	103,105	1
Acetone	43	58	1
Isopropyl Alcohol	45	43	1
1,1-Dichloroethene	61	96	1
Freon 113	101	103,151	1
Methylene Chloride	49	84,86	1
Carbon Disulfide	76	44,78	1
Trans-1,2-Dichloroethene	96	61,98	1
Methyl Tert Butyl Ether	73	41	1
Vinyl Acetate	43	86	1
1,1-Dichloroethane	63	65	1
Methyl Ethyl Ketone	72	43	1
Hexane	57	41,43	1
Cis-1,2-Dichloroethene	96	61,98	1
Ethyl Acetate	43	61,70	1
Chloroform	83	85,47	1
Tetrahydrofuran	42	41,72	1
1,1,1-Trichloroethane	97	99,61	1
1,2-Dichloroethane	62	64	1
Benzene	78	77,50	1
Carbon Tetrachloride	117	119	1
Cyclohexane	56	84,41	1
Heptane	43	41	1
1,2-Dichloropropane	63	41,62	1
Trichloroethene	130	132,95	1

ATTACHMENT III (continued) - Characteristic Ions For Target Compounds

Compound	Primary Ion	Secondary Ion(s)	Internal Standard Group
Bromodichloromethane	83	85	1
Napthalene	128	127	1
Methyl Isobutyl Ketone	43	58,100	1
Cis-1,3-Dichloropropene	75	39,77	1
Trans-1,3-Dichloropropene	75	39,77	1
Toluene	91	92	1
1,12-trichloroethane	97	83,61	1
Methyl Butyl Ketone	43	58	2
Dibromochloromethane	129	127	2
1,2-Dibromoethane	107	109	2
Tetrachloroethene	166	164,131	2
Chlorobenzene	112	77,114	2
Ethyl Benzene	91	106	2
M,P,& O Xylene	91	106	2
Bromoform	173	171	2
Styrene	104	78,103	2
1,1,2,2-Tetrachloroethane	83	85	2
4-Ethyltoluene	105	120,79	2
1,3,5-Trimethylbenzene	105	120	2
1,2,4-Trimethylbenzene	105	120	2
1,3-Dichlorobenzene	146	111,148	2
Benzyl Chloride	91	126	2
1,4-Dichlorobenzene	146	148,111	2
1,2-Dichlorobenzene	146	111,148	2
1,2,4-Trichlorobenzene	180	182,184	2
Hexachlorobutadiene	225	227,223	2
1,4-Difluorobenzene	114	88	IS #1
Chlorobenzene	117	82	IS #2
Hexane-d14 (surr)	66	64	1
Toluene-d8 (surr)	98	100	1
1,4-Dichlorobenzene-d4 (surr)	150	152	2

ATTACHMENT IV - Calibration of THC as Gas

IV-1 THC as gas is calibrated by using the same calibration runs that are used for all other compounds, as well as using the same acceptance criteria.

IV-2 The original calibration files are copied to a target batch. This does not change the raw data in any way, it merely allows the same data to be processed against two different methods

IV-3 The area response is obtained by summing the area in the total ion chromatogram from the first eluting compound of interest till the end of the run. The internal standard is included as part of this value, the response factor is not calculated using the internal standard method. It is solely based on area response and calibration concentration

IV-4 The calibration concentration at each level is obtained by summing the values of the individual compounds present in the calibration standard.

IV-5 A response factor is obtained as detailed earlier in this SOP. Calibration criteria are the same as stated earlier in this SOP.

IV-6 Custom THC values may be obtained and are noted as such on final reports. These custom values can be based on calibrating using a select list of compounds or a select time frame for example. Requests for these custom values are to be evaluated on an individual basis for analytical feasibility.

ATTACHMENT V - Canister Dilution Factors (6L)

Initial Pressure Units (inches Hg or PSIG)	Initial Pressure	Initial Pressure Converted to PSIA	Final Pressure (PSIG)	Final Pressure Conver. to PSIA	Dilution Factor
Hg	0	14.70	5	19.7	1.34
Hg	-1	14.21	5	19.7	1.39
Hg	-2	13.72	5	19.7	1.44
Hg	-3	13.23	5	19.7	1.49
Hg	-4	12.74	5	19.7	1.55
Hg	-5	12.24	5	19.7	1.61
Hg	-6	11.75	5	19.7	1.68
Hg	-7	11.26	5	19.7	1.75
Hg	-8	10.77	5	19.7	1.83
Hg	-9	10.28	5	19.7	1.92
Hg	-10	9.79	5	19.7	2.01
Hg	-11	9.30	5	19.7	2.12
Hg	-12	8.81	5	19.7	2.24
Hg	-13	8.31	5	19.7	2.37
Hg	-14	7.82	5	19.7	2.52
Hg	-15	7.33	5	19.7	2.69
Hg	-16	6.84	5	19.7	2.88
Hg	-17	6.35	5	19.7	3.10
Hg	-18	5.86	5	19.7	3.36
Hg	-19	5.37	5	19.7	3.67
Hg	-20	4.88	5	19.7	4.04
Hg	-21	4.39	5	19.7	4.49
Hg	-22	3.89	5	19.7	5.06
Hg	-23	3.40	5	19.7	5.79
Hg	-24	2.91	5	19.7	6.76
Hg	-25	2.42	5	19.7	8.14
Hg	-26	1.93	5	19.7	10.21
Hg	-27	1.44	5	19.7	13.69
Hg	-28	0.95	5	19.7	20.79
Hg	-29	0.46	5	19.7	43.17
PSIG	1	15.7	5	19.7	1.25
PSIG	2	16.7	5	19.7	1.18

Canister Dilution Equation:

DF = (Pf + 14.7) / Pi + 14.7)
Pi = Pressure reading of canister prior to pressurization (psig)
Pf = Pressure reading of canister after pressurization (psig)
DF = Dilution factor

To convert Hg to psig:
Divide by 2.036

PSIG reading is converted to One Atmosphere:
One Atmosphere = 14.7 psig = 29.21 inches of Hg

ATTACHMENT V (continued) - Canister Dilution Factors (1L)

Initial Pressure Units (inches Hg or PSIG)	Initial Pressure	Initial Pressure Converted to PSIA	Final Pressure (PSIG)	Final Pressure Conver. to PSIA	Dilution Factor
Hg	0	14.7	10	24.7	1.68
Hg	-1	14.21	10	24.7	1.74
Hg	-2	13.72	10	24.7	1.80
Hg	-3	13.23	10	24.7	1.87
Hg	-4	12.74	10	24.7	1.94
Hg	-5	12.24	10	24.7	2.02
Hg	-6	11.75	10	24.7	2.10
Hg	-7	11.26	10	24.7	2.19
Hg	-8	10.77	10	24.7	2.29
Hg	-9	10.28	10	24.7	2.40
Hg	-10	9.79	10	24.7	2.52
Hg	-11	9.30	10	24.7	2.66
Hg	-12	8.81	10	24.7	2.80
Hg	-13	8.31	10	24.7	2.97
Hg	-14	7.82	10	24.7	3.16
Hg	-15	7.33	10	24.7	3.37
Hg	-16	6.84	10	24.7	3.61
Hg	-17	6.35	10	24.7	3.89
Hg	-18	5.86	10	24.7	4.22
Hg	-19	5.37	10	24.7	4.60
Hg	-20	4.88	10	24.7	5.06
Hg	-21	4.39	10	24.7	5.63
Hg	-22	3.89	10	24.7	6.34
Hg	-23	3.40	10	24.7	7.26
Hg	-24	2.91	10	24.7	8.48
Hg	-25	2.42	10	24.7	10.20
Hg	-26	1.93	10	24.7	12.80
Hg	-27	1.44	10	24.7	17.17
Hg	-28	0.95	10	24.7	26.07
Hg	-29	0.46	10	24.7	54.12
PSIG	1	15.7	10	24.7	1.57
PSIG	2	16.7	10	24.7	1.48

Canister Dilution Equation:

DF = (Pf + 14.7) / Pi + 14.7)
Pi = Pressure reading of canister prior to pressurization (psig)
Pf = Pressure reading of canister after pressurization (psig)
DF = Dilution factor

To convert Hg to psig:
Divide by 2.036

PSIG reading is converted to One Atmosphere:
One Atmosphere = 14.7 psig = 29.21 inches of Hg

ATTACHMENT V (continued) - Canister Dilution Factors (1L)

AIR CANISTER DILUTIONS

When a sample is over the linear range of calibration for a compound of interest, several compounds of interest, or the matrix of the sample interferes with internal standard detections, a dilution is performed.

SYSTEM DILUTION
The pre-concentrator uses a digital mass flow controller to pull volume of the air sample onto the system.

1x = 500cc
2x = 250cc
5x = 100cc
10x = 50cc
20x = 25cc

SERIAL DILUTION
For samples that may require a dilution greater than 20x, the lab performs serial dilutions by emptying the pressurized air in the sample back to ambient conditions (0psig) and refilling the can to 15psig.
This doubles the volume once inside the can and is a 2x

As you multiply this process, the resultant dilution factor is multiplied out.

1. Flush to 0psig fill to 15 = **2x**
2. Flush to 0 and fill again to 15 = **4x**
3. **8x**
4. **16x**
5. **32x**
6. **64x**

ATTACHMENT VI - Air Laboratory Standard Preparation Procedures

CALIBRATION STANDARD

The calibration stock standard is purchased in the form of a pressurized cylinder from SPECTRA GASES, Inc, or equivalent. This is a custom mix that includes all compounds of interest at 1ppmv.

TO15 Standard Preparation

Standards are prepared in a 6L or 15L summa canister that has been evacuated to less than 150 mTorr. The canister is humidified with 50 µl of deionized water. A 1000cc gas tight syringe is filled with a desired volume of TO15 stock standard, depending on the desired final concentration of the summa canister. The summa canister is then pressurized to 30 psig (3 atm) with clean nitrogen from Praxair.

The standard ID, date created, analyst initials, canister number, canister volume, stock standard ID, volume used, water volume added, final pressure in psig, final concentration in ppbv and expiration date are recorded in the standard preparation logbook.

Second Source Verification

The second source stock standard is purchased in the form of a pressurized cylinder from a source independent of the calibration mix (Custom Gas, or equivalent). This includes all compounds of interest at 1ppmv.

The second source standard is prepared in a 6L or 15L summa canister following the same method as the TO15 20.0 ppbv standard.

Canister Volume (L)	Canister Final Pressure (psig)	Canister Final Pressure (atm)	Canister Pressurized Volume (L)	Standard Volume (cc)	Standard Volume (L)	Final Standard Concentration (ppmv)	Final Standard Concentration (ppbv)
6	30	3.04	18.24	36	0.036	0.002	2.00
15	30	3.04	45.6	90	0.09	0.002	2.00
6	30	3.04	18.24	360	0.36	0.020	20.00
15	30	3.04	45.6	900	0.9	0.020	20.00

*The Pressurized canister volume can be obtained from Boyle's Law, stating $P_1V_1=P_2V_2$. At 3.04 atm, a 15L cylinder occupies the same volume as a 45.6L cylinder at 1.00 atm. 900 cc of a standard is put into the pressurized canister creating a 0.90L/45.6 L dilution factor to result in the standard to determine the final concentration in ppbv.

ATTACHMENT VI (continued) - Air Laboratory Standard Preparation Procedures

Internal Standard/ Surrogate/ BFB Standard 200ppbv:

The internal, surrogate, and bfb standards are purchased as neat standards from specific vendors; such as Chem-Service, Sigma-Aldrich or equivalent. The standard is purchased in a 1.0mL vial with the following components:

Hexane D4	239ul
Toluene D8	195ul
Chlorobenzene D5	186ul
1,4 Difluorobenzene	179ul
BFB	201ul
1,4 Dichlorobenzne D4	0.277g

To prepare the internal standards, 25µl of neat standard is added to a clean 2L flask. The flask is then heated at 55-75°C for 30 min. Following this, the flask is removed from the heat and allowed to cool to ambient temperature. A 20cc aliquot of the volatilized internals is spike from the 2L flask into a clean, humified and evacuated 15L canister. The 15L canister is then filled to positive 30 psig with clean nitrogen, resulting in a final concentration of 200ppbv for all components. Below is a table summarizing this process:

Compound	Volume in neat standard (mL)	Density (g/ml)	Mass (g)	Molecular Weight (g/mol)	Molar value	mol in 25 ul	Flask concentration (ppmv)	Final can Concentration (ppbv)
Chlorobenzene-d5	0.186	1.157	0.215	117.59	$1.83x10^{-03}$	$3.679x10^{-05}$	450	200
1,4-difluorobenzene	0.179	1.17	0.209	114.09	$1.84x10^{-03}$	$3.690x10^{-05}$	450	200
BFB	0.201	1.593	0.320	175	$1.83x10^{-03}$	$3.678x10^{-05}$	450	200
1,4-Dichlorobenzene-d4			0.277	151.03	$1.83x10^{-03}$	$3.686x10^{-05}$	450	200
n-hexane-d14	0.239	0.767	0.183	100.26	$1.83x10^{-03}$	$3.675x10^{-05}$	450	200
toluene-d8`	0.195	0.943	0.184	100.19	$1.84x10^{-03}$	$3.689x10^{-05}$	450	200

ATTACHMENT VII - Procedures For Analyzing MPCA Samples

VII-1 Samples must be carefully monitored for carryover from previous samples with large detections. Analysts and data reviewers need to verify that each analysis has been evaluated for potential carryover.

- If a compound of interest has an on-column concentration that is greater than 10% of the previous sample, it is assumed that this value is not due to carryover.
- If the compound of interest has an on-column concentration between 2 and 10% of the previous sample, then the analyst carefully examines other factors relating to sample analysis (i.e. the concentration of related components, the overall concentration of constituents in each sample, etc.). When in doubt, the analyst must re-analyze the sample to confirm that the results are not due to carryover.
- When the compound of interest has an on-column concentration which is less than 2% of the previous sample's concentration, but greater than the method reporting limit, the sample must be analyzed to confirm or eliminate possible carryover.

VII-2 Sample duplicate analysis must be performed at a minimum of 1 in 10 samples analyzed.

VII-3 The relative detection limit for MPCA samples is 0.200 ppbv for all analytes except m&p xylene which has a relative detection limit of 0.400 ppbv.

ATTACHMENT VIII - Procedure for Tedlar Bags

Transfer of Tedlar Bags to SUMMA Canisters

In the event that a sample is collected into a tedlar bag, the client has two days to get the bag to the facility for analytical testing. Pace Analytical Services recognizes a two day holding time for all samples collected in tedlar bags. Upon receipt at the laboratory, the sample in the tedlar bag is transferred into a batch certified, evacuated one liter SUMMA canister for analysis. The sample is subsequently analyzed by the appropriate method within 28 days of transfer.

Procedure for transfer:

- Tedlar bag is received and logged for analysis by Pace Analytical Services
- The sample is delivered to the Air Lab, and the laboratory numbers assigned to the sample is recorded in a logbook (as delivered; see Attachment IX).
- The bag is connected to a clean, evacuated canister (105mTorr).
    - The tip of the bag valve is placed into tubing, connected by a ¼" nut to the sample valve of the canister, secured with a wrench to insure all sample is pulled into the can.
- The bag is opened first. Second, the can is opened.
    - By opening the canister second, the sample is transferred into the can through vacuum (since the can is evacuated to 150mTorr, and the bag is at ambient room pressure).
- After the sample is transferred the sample data and canister number, time and date, is recorded into the transfer logbook (Attachment X).
- Sample is submitted to the laboratory for analysis.
- A data qualifier is added to the report, notifying the client of the transfer.

ATTACHMENT IX - Tedlar Sign-off Logbook (example)

Pace Analytical

Tedlar Signoff Logbook

Date	Time	Project Number	Sample Number(s)	Method	Initials

ATTACHMENT X - Tedlar Bag Transfer Log (example)

Pace Analytical

Tedlar Bag Transfer Log

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Sample ID	Can ID	Date Collected	Date when Tedlar Bag was evacuated to the can	Comments

O107 Rev.01 (20Nov2006)
Pace Analytical Services, Inc. – MN

Reviewed by:____________________
Date:____________________

ATTACHMENT XI – Common Logbook Abbreviations

RR	**Reanalysis for previously analyzed sample**
DIL	**Dilution for over-range compounds from a previously reported sample**
CONF	**Confirms results from a previously analyzed sample**
C/O	**Possible carryover from a prior sample**
OK	**Analysis is acceptable and sample is reported**

ATTACHMENT XII – Determination of Air Phase Petroleum Hydrocarbons (APH)

This method is designed, based on the Massachusetts APH method, to measure the gaseous-phase concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in air and soil gas. Volatile aliphatic hydrocarbons are collectively quantitated within two carbon number ranges: C_5 through C_8, and C_9 through C_{12}. Volatile aromatic hydrocarbons are collectively quantitated within the C_9 to C_{10} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 28°C and 245°C. This is a performance-based method. Modifications to this method are permissible, provided that adequate documentation exists, or has been developed, to demonstrate an equivalent or superior level of performance.

Collective Aliphatic/Aromatic ranges: Relative Response Factors are calculated for C_5-C_8 Aliphatic Hydrocarbons and C_9-C_{12} Aliphatic Hydrocarbons based upon a correlation between the TOTAL mass of aliphatic APH Component Standards eluting within the range of interest and the total ion area count. A Relative Response Factor is calculated for C_9-C_{10} Aromatic Hydrocarbons based upon a correlation between the TOTAL mass of aromatic APH Component Standards eluting within this range and the total area count of extracted ions 120 and 134. Specified APH Component Standards are designated "marker" compounds to define the beginning and end of the hydrocarbon ranges.

- **C_5 through C_8 Aliphatic Hydrocarbon**s are defined as all aliphatic hydrocarbon compounds which elute from isopentane to just before n-nonane (C_9).
- **C_9 through C_{12} Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute from n-nonane to just after 1-methylnaphthalene.
- **C_9 through C_{10} Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds which elute from just after o-xylene to just after 1-methylnaphthalene, excluding naphthalene and 2-methylnaphthalene, which are quantitated and evaluated separately as Target APH Analytes.

Hydrocarbon Range	Beginning Marker	Ending Marker
C_5-C_8 Aliphatic Hydrocarbons	0.1 min. before isopentane	0.01 min. before n-Nonane
C_9-C_{12} Aliphatic Hydrocarbons	0.01 min. before n-Nonane	0.1 min. after 1-Methylnaphthalene
C_9-C_{10} Aromatic Hydrocarbons	0.1 min. after o-xylene	0.1 min. after 1-Methylnaphthalene

Standard Information: All APH standards are purchased as 30 component mixtures from a known vendor, such as SPEX CertiPrep or O2Si, in methanol.

Initial Calibration (*Suggested Parameters*)

- Standard Concentration: All components 10 ppmv
- Prepare a **20 ppbv** working standard by adding 36cc to a clean, evacuated 6L canister. Fill to 30psig.

Second Source Verification

- Standard Concentration: Components range from 30-70ug/ml
- Prepare working standard by adding 7.2ul to a clean, evacuated 6L canister. Fill to 30psig.

ATTACHMENT XII (continued) – Determination of Air Phase Petroleum Hydrocarbons (APH)

Initial Calibration and SSV Table:

	Volume (cc)	C5-C8	C9-C12	C9-C10
ICAL-1	10	5.2	6.4	2.4
ICAL-2	25	13	16	6
ICAL-3	50	26	32	12
ICAL-4	125	65	80	30
ICAL-5	250	130	160	60
ICAL-6	500	260	320	120
SSV	250	165	145	59

all expressed in ppbv

Component Mixture		Ions	
Compound	**CAS NO**	**Quant**	**Qual.**
1,3-Butadiene	106990	54	39
Isopentane	78784	43	42
MTBE	1634044	73	41
n-Hexane	110543	57	41/43
Benzene	71432	78	77/50
Cyclohexane	110827	56	84/41
2,3-Dimethylpentane	565593	56	43
n-Heptane	142825	43	41
Toluene	108883	91	92
n-Octane	111659	43	85/57
Ethylbenzene	100414	91	106
2,3-Dimethylheptane	3074713	43	84/85
m-Xylene	108383	91	106
p-Xylene	106423	91	106
o-Xylene	95476	91	106
n-Nonane	111842	43	57
Isopropylbenzene	98828	105	120
1-Methyl-3-ethylbenzene	620144	105	120
1,3,5-Trimethylbenzene	108678	105	120
n-Decane	124185	57	85
1,2,3-Trimethylbenzene	526738	105	120
p-Isopropyltoluene	99876	119	105
Indene	95136	115	116
Butylcyclohexane	1678939	83	55
n-Undecane	1120214	57	42
Naphthalene	91203	128	127
n-Dodecane	112403	57	43
Hexylcyclohexane	4292755	83	82
2-Methylnaphthalene	91576	142	141
1-Methylnaphthtalene	90120	142	141

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STANDARD OPERATING PROCEDURE

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN WATER

Reference Methods: EPA 524.2

Local SOP Number:	S-MN-O-546-rev.12
Effective Date:	Date of Final Signature
Supersedes:	S-MN-O-546-rev.11

APPROVALS

Laboratory General Manager — Date: 08 Mar 2017

Laboratory Quality Manager — Date: 08 Mar 2017

PERIODIC REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE PREVIOUS APPROVAL.

Signature	Title	Date

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1. PURPOSE/IDENTIFICATION OF METHOD

1.1. The purpose of this Standard Operating Procedure (SOP) is to define the process and conditions involved in analyzing water samples by GC/MS to determine volatile organic compounds based on EPA Method 524.2.

2. SUMMARY OF METHOD

2.1. The volatile organic compounds are introduced into the gas chromatograph by the purge-and trap method or by direct injection. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and back flushed with helium to desorb trapped sample components. The analytes are directly desorbed onto a narrow bore capillary column connected to a split/splitless injection port. The column is temperature programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph.

2.2. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is quantitated by relating the MS response for an appropriate selected ion produced by that compound to the MS response for an appropriately selected ion produced by an internal standard.

3. SCOPE AND APPLICATION

3.1. **Personnel**: The policies and procedures contained in this SOP are applicable to all personnel involved in the analytical method process of purge and trap GC/MS systems.

3.2. **Parameters**: This SOP applies to a wide range of organic compounds, including the four trihalomethane disinfection products that have sufficient volatility and low water solubility to be removed from water samples with purge and trap procedures. For a list of analytes that can be analyzed with this method, see Attachment I.

4. APPLICABLE MATRICES

4.1. This SOP is applicable to the identification and measurement of purgeable volatile organic compounds in surface water, ground water and drinking water in any stage of treatment.

5. LIMITS OF DETECTION AND QUANTITATION

5.1. The reporting limit or Limit of Quantitation (LOQ) for all analytes ranges from 0.5 - 40.0 µg/L for this method. All current MDLs and LOQs are listed in the LIMS and are available by request from the Quality Manager.

6. INTERFERENCES

6.1. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials can be sources of compounds which can concentrate in the trap during the purging. Analyses of blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should investigate the source of contamination and correct it. Subtracting blank values from sample results is not permitted. If the laboratory feels that a sample results is a false positive due to these sources, this should be fully explained in text accompanying the uncorrected data.

6.2. Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing of the purging apparatus and sample syringes with

two portions of organic-free reagent water between samples. After analysis of a sample containing high concentrations of volatile organic compounds, one or more method blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high concentrations of compounds being determined, it may be necessary to wash the purging device with methanol, rinse it with organic-free reagent water, and then dry the purging device in an oven less than 120°C. In extreme situations, the whole purge and trap device may require dismantling and cleaning, typically a methanol back flush followed by a DI water back flush. Screening the sample prior to analysis is recommended to prevent system contamination. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique using a flame ionization detector or by analyzing the sample at a dilution by purge and trap GC/MS.

6.3. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank is prepared using HPLC grade, organic-free, water (or pre-tested, boiled and/or purged DI water) and carried through the sampling and handling protocol or pre tested, boiled, deionized water can serve as a check on such contamination. Trip blanks may also be purchased premade, refer to the *Bottle Preparation* SOP, *S-MN-C-003*, or equivalent replacement.

7. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

7.1. Table 7.1 Sample Collection, Preservation and Storage.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	A minimum of duplicate 40 mL VOA vials	Sodium thiosulfate or 25mg of ascorbic acid, with no headspace. If the samples contain residual chlorine, it should have been dechlorinated with sodium thiosulfate before being preserved in the vials.	<6°C, but above freezing	Must be analyzed within 14 days of collection.
		If the samples are not known to be from a chlorinated source, absorbic acid or sodium thiosulfate may not be needed. Acidified with 1:1 hydrochloric acid (HCl) to pH<2; no headspace. DO NOT use for THMs. If the samples contain residual chlorine, it should have been dechlorinated with sodium thiosulfate before being preserved in the vials.	<6°C, but above freezing	Must be analyzed within 14 days of collection.
		Unpreserved for THM analysis request	<6°C, but above freezing	Must be analyzed within 24 hours of collection.
Trip blank	Minimum of one per project of VOA analysis. It is recommended to use the same lot of preservative for trip blanks and samples	Preserve the same as the samples as outlined above	<6°C, but above freezing	Same as the samples

8. DEFINITIONS

8.1. Definitions of terms found in this SOP are described in the Pace Analytical Services Quality Manual, Glossary Section.

9. EQUIPMENT AND SUPPLIES (INCLUDING COMPUTER HARDWARE AND SOFTWARE)

9.1. Table 9.1 Equipment and Supplies.

Supply	Description	Vendor/ Item # / Description
Sample Vials	40 mL glass with Teflon-lined septa and screw caps	C&G Unpreserved Vials NC9879693 or equivalent
Volumetric Flasks	Class A in Various sizes, e.g. 5 mL, 10 mL, 50 mL, 100 mL, 250 mL, 500 mL and 1000 mL with ground glass stopper	Fisher Scientific or equivalent replacement
Amber Vials	Various sizes, e.g. 1 mL, 4 mL and 12 mL with Teflon line screw caps	Fisher Scientific or equivalent replacement
Microsyringes	10, 25, 50, 100, 250, 500 and 1000 µL	Hamilton or equivalent replacement
Syringes	5.0, 10, 25, or 50 mL gas tight with shut off valve	Hamilton, or equivalent replacement
Disposable pipets	Pasteur	Fisher Scientific 13-678-31J or equivalent replacement
pH test strips	The range of 0-14	Fisher Scientific or equivalent replacement
Autosampler	Archon 5100 and EST Archon 8100, or Centurion w/s	Varian or Centurion or equivalent replacement
Sample Concentrator	EST Encon Envolution(EV) Concentrator, Tekmar (Lab Sample Concentrator) LSC 3100, LSC 3000	Encon or Tekmar or equivalent replacement
Purging Chamber	Designed to accept 10 mL sample with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles 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.	Varian or Centurion or equivalent replacement
Trap Packing	Any of these traps may be used if the trap packing materials do not introduce contaminants into the analysis and the data generated using the trap meets the initial and continuing calibration technical acceptance criteria of this method.	Tenax/silica gel/carbon trap, tenax/silica gel/carbon/OV-1 trap, and a Vocarb 3000 trap, or equivalent replacement.
Desorber	capable of rapidly heating the trap to the manufacturer's recommended temperature for desorption, typically 180°C to 260°C, depending on the trap chosen	EST EV, Tekmar LSC-3100, LSC 3000 or equivalent replacement
Gas Chromatography/Mass Spectrometer (GC/MS)	An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection (Hewlett Packard HP 6890 or equivalent)	Agilent 6890 or equivalent replacement

GC Column	20 m x 0.18 mm ID x 1.0 µm film thickness capillary column; 30 m x 0.25 mm ID x 1.4 µm film thickness capillary column	Restek VMS-Rtx, or equivalent
Mass Spectrometer (MS)	Capable of scanning from 35 to 300 amu every 2 seconds or less, using 70 Electron volts (nominal) in the electron impact (EI) ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Bromofluorobenzene (BFB) which meets all of the criteria in 11.2 when 25 ng or less of the GC/MS tuning standard (BFB) is transferred onto the column. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC	Agilent 5973N MSD or equivalent replacement
GC/MS Interface	The GC is interfaced to the MS with an all glass enrichment device and an all glass transfer line. Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria may be used. If a 0.18-0.32 mm ID capillary column is used, it is positioned directly into the ion source and this GC/MS interface acts only as a heated connection, not as an enrichment device	Agilent
Data System	A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available	Hewlett-Packard Chemserver
Data processing software	See master software list for current version	Target 4.1, or equivalent replacement
Data reporting software	Laboratory information management system (LIMS)	Horizon, also referred to as Epic Pro; or equivalent replacement
Data review and package software	Compiles pdf images of all the data to be available for package generation and secondary review	Gandalf, see master software list for revision

9.2. Recommended operating conditions for the 3000 Concentrator

Purge ready/standby temp	100˚C
Purge temp	20˚C
Purge time	11min

Desorb preheat temp	245˚C
Desorb time	1-3min
Desorb temp	250˚C
Bake temp	270˚C
Bake time	7-10min
Bake bypass	Off
BGB bypass time	2min
MCS Bakeout temp	40˚C
Transfer line temp	150˚C
Line temp	150˚C
Valve temp	150˚C
Mount temp	40˚C
MCS line temp	40˚C

10. REAGENTS AND STANDARDS

10.1. Table 10.1 Reagents and Standards.

Reagent/Standard	Description	Vendor/ Item # / Description
Organic-free Water (OFW)	Deionized. Verify that background levels of volatile compounds are acceptable by analysis	Verify that background levels of volatile compounds are acceptable by analysis
Methanol (MeOH)	CH_3OH - Fisher Purge and Trap grade or equivalent, demonstrated to be free of analytes. Store apart from other solvents	Fisher Scientific A453-1 or equivalent replacement
Surrogate Standard	10,000mg/L	O_2Si -120290-04-P-(8260 IS/SS Soln)
Stock Standard	Stock solutions are typically purchased as certified solutions. Multiple stock standards can be combined (diluted) to yield one working standard. 1000-40,000mg/L	O_2Si - 122311-02-02 (8260 Gases) O_2Si –125872-08 (Custom 96-5-) O_2Si - 125875-05–(Reactive 5-81) or equivalent
Internal Stock Standard	10,000mg/L; 10,000-100,000mg/L	O_2Si -120290-04-P-(8260 IS/SS Soln); Chemservice - SP-8930-4710CSZ (1,4-dioxane d8 and acetone d6)
Tuning Standard	10,000mg/L	O_2Si -120290-04-P-(8260 IS/SS Soln)
Initial Calibration Verification Stock Standard	1000-40,000mg/L	O_2Si - 122311-02-02-SS (8260 Gases SS) O_2Si - 125872-08-SS – (Custom 96-5 SS SS) O_2Si - 125875-05-SS – (Reactive 45-81SS) or equivalent
Anti-Foaming Agent	Add 2g to 42 mL of DI water and mix vigorously. The solution must be gently shaken solution prior to use. If anti-foam is used for samples, injection 100-200uL of anti-foam solution into the vial	Dow Corning 1520-US Antifoam or equivalent replacement

10.2. **Working Standard Dilutions and Concentrations**

Standard	Standard(s) Amount	Solvent	Solvent Volume	Final Total Volume	Final Concentration

Intermediate Tune Solution	500 µL	Methanol	100 mL	50 µg/mL	Intermediate Tune Solution
Tune	5 µL	Water	5mL	50 µg/L	Tune
Calibration Working Standard	0.5mL of 1000mg/L-40,000mg/L	Methanol	9.5mL methanol	10mL	50-2000 µg/mL(nominal conc 100ug.mL)
Calibration Std 1	0.5 µL	Methanol	249.999 water	250 mL	0.2 µg/L
Calibration Std 2	1.0 µL	Methanol	249.9995 water	250 mL	0.4 µg/L
Calibration Std 3	1.0 µL	Methanol	99.999 water	100 mL	1 µg/L
Calibration Std 4	4.0 µL	Methanol	99.996 water	100 mL	4 µg/L
Calibration Std 5	10.0 µL	Methanol	99.99 water	100 mL	10 µg/L
Calibration Std 6	20.0 µL	Methanol	99.98 water	100 mL	20 µg/L
Calibration Std 7	50.0 µL	Methanol	99.95 water	100 mL	50 µg/L
Calibration Std 8	100.0 µL	Methanol	99.90 water	100 mL	100 µg/L
Calibration Std 9	250.0 µL	Methanol	99.75 water	100 mL	250 µg/L
Surrogate Working Standard for Archon	0.5mL of 10,000mg/L	Methanol	19.5mL methanol	20mL	250 µg/mL
Surrogate Working Standard for Centurion	0.5mL of 10,000mg/L	Methanol	99.5mLmethanol	100mL	50 µg/mL
Internal Standard Working Standard for Archon	0.5mL of 10,000mg/L; 0.5mL of 10,000 to 100,000mg/L	Methanol	19.5mL methanol	20mL	250 µg/mL (1,4-dioxane-d8 is at 5000 µg/mL)
Internal Standard Working Standard for Centurion	0.5mL of 10,000mg/L; 0.5mL of 10,000 to 100,000mg/L	Methanol	99.5mLmethanol	100mL	50 µg/mL (1,4-dioxane-d8 is at 1000 µg/mL)
Continuing Calibration Verification Standard at 50ppb	100uL of working std	Water	199.9mL of water	200mL	50ug/mL
Continuing Calibration Verification Standard at 20ppb	50uL of working std	Water	249.95mL of water	250mL	20ug/mL

10.3 All standards, blanks, spikes, and samples must be analyzed using the same conditions. A set of at least five calibration standards containing the method analytes and surrogates are needed (six standards are necessary for quadratic curve fits). One calibration standard should contain each analyte at a concentration at or below the reporting limit for that compound; the other calibration standards should contain analytes at concentration that define the range of the method. To prepare a calibration standard, add an appropriate volume of standard solution to organic-free reagent water in a volumetric flask. Using a microsyringe, rapidly inject the standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times. Transfer the standard to a 40 mL VOA vial and load into the Autosampler. If ICAL or CCVs are not used immediately they must be stored at 0 to 6 degrees Celsius in a cooler which does not house samples for up to one day from the day they were made.

11. CALIBRATION AND STANDARDIZATION

11.1. Table 11.1 Calibration and Standardization.

Calibration Metric	Parameter / Frequency	Criteria	Comments
Tune	4-Bromofluorobenzene (BFB) at 25 ng or less is injected prior to sample analysis every 12 hours	See criteria in 11.2	The spectra used for evaluation is generated using a Target method that takes the average of three scans across the BFB peak and makes a background subtraction. The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration acceptance criteria can be met without interferences
Calibration Curve Fit	Average Linear Regression Quadratic Regression Quadratic needs 6 point minimum	RSD ≤ 20% r ≥ 0.990 $r^2 \geq 0.990$	If not met, try non-linear regression fit. If still not met, remake standards and recalibrate and verify before sample analysis.
Second Source Verification Standard (ICV)	Immediately after each initial calibration	% Recovery ±30% unless otherwise specified in a QAPP	If the requirements for ICV are not met, verify the standard preparation and if there are any apparent issues with the initial analysis. Reanalyze one more time. Only two injections of the same standard are permitted back to back prior to recalibrating the instrument.
Continuing Calibration Verification (CCV)	Prior to the analysis of any samples or every 12 hours, whichever is more frequent.	% Recovery ±30%	If the requirements for continuing calibration are not met, review for standard preparation errors. Remake accordingly. Reanalyze one time, if the criteria still fails; perform any necessary maintenance and recalibrate the instrument prior to analysis.
Internal Standards	All analytical runs	Retention time must be ±30 seconds of any internal standard from the CCV; the response factor must be within -50% to 200%. Client, QAPP, or state requirements may supersede this requirement.	The chromatographic system must be inspected for malfunctions and corrections must be made.
Reporting Limit Verification	A standard at the reporting limit concentration. Required following the ICAL and every 30 days during the life of the ICAL for samples originating in	± 40%	If the requirements are not met, review for standard preparation errors. Remake accordingly. Reanalyze one time, if the criteria still fails review the data quality objectives of the samples. If the DQOs can be met by raising the

	MN.		reporting limit to the next calibration level that meets the criteria, adjust the reporting limit accordingly and continue analysis. If the DQOs cannot be met, recalibrate the instrument.

11.2. Each GC/MS system must be a hardware-tuned using perfluorotributylamine (PFTBA) and must also meet the criteria below for a 5-50-ng injection of 4-bromorfluorobenzene. Analyses must not begin until these criteria are met.

BFB Key Ions and Ion Abundance Criteria by method 524.2

Mass	Ion Abundance Criteria
95	Base Peak, 100% relative abundance
50	15.00 - 40.00% of m/z 95
75	30.00 - 66.00% of m/z 95
96	5.00 - 9.00% of m/z 95
173	Less than 2.00% of m/z 174
174	50.00-120% of m/z 95
175	5.00 - 9.00% of m/z 174
176	95.00 to 101.00% of m/z 174
177	5.00 - 9.00% of m/z 176

Note: All ion abundance must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent.

11.3. Tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured. See Section 14 for the RF calculation.

12. PROCEDURE

12.1. BFB tuning criteria and daily GC/MS calibration criteria must be met before analyzing samples.

12.2. Sample vials are loaded onto the auto-sampler.

12.3. The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample vial is sealed.

12.3.1. Dilutions may be made in volumetric flasks of various sizes. Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions. Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask. Refer to Attachment I for common dilution factors.

12.3.2. Inject the proper aliquot of sample into the flask. Dilute the sample to the mark with organic-free reagent water. Cap the flask and invert three times. Once sample dilution is completed, the pH of the un-diluted sample must be taken with pH paper. If the pH is greater than 2 the sample must be footnoted. Repeat above procedure for additional dilutions.

12.3.3. Fill the vial with diluted sample and load onto the autosampler.

12.4. The autosampler adds the internal standard spiking solution and the surrogate spiking solution to the 5mL sample aliquot. The amount added by the autosampler should be equivalent to the concentration of 50 µg/L of each surrogate, 50 µg/L for the internal standards. The archon accomplishes this by adding the internal standard and surrogate solution utilizing a 1 µL loop, the centurion w/s adds 5 µL of the solution. If 10mL sample aliquot is used, the amount added by the autosampler should be

equivalent to the concentration of 25 µg/L of each surrogate, 25 µg/L for the internal standards(1,4 dioxane d8 is at a concentration of 2500 µg/mL).

12.5. If the initial analysis of sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated ions from a compound, this analysis may be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences. Alternately, samples loaded on an auto-sampler can be accepted after a subsequent sample is shown to be free of carry-over contamination or if the detection is 10x greater than the carryover detection. Carryover in P&T systems can vary for instrument to instrument depending on the condition of the equipment. Analysts review the carryover after the upper level of the initial calibrations and after the ICV, in addition they monitor the carryover daily on the system blanks ran which is generally ran after QC samples. It is common for the laboratory to run multiple blanks after an initial calibration to monitor the carryover and ensure the ICV does not have carryover affecting the % recoveries. Daily, it is common for the laboratory to run system blank before the method blank. This is to help determine if there is a contamination coming from the system itself or if contamination occurred during the sample preparation phase.

12.6. All samples must be thoroughly reviewed when sample concentrations exceed 20 µg/L to ensure low level carryover is not occurring into subsequent analyses.

12.7. Once sample analysis is completed, the pH and residual chlorine must be checked with test strips and recorded in the instrument run logbook. If the pH is greater than 2 and the holding time is past 24 hours, the client must be notified via the project manager and the data qualified at a minimum, exception would be if THM's only. Note any residual chlorine presence on the instrument runlog and qualify data accordingly.

12.8. Qualitative Analysis.

12.8.1. An analyte is identified 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 should be obtained on the user's GC/MS. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component, and (2) correspondence of the sample component and the standard component mass spectrum.

12.8.1.1. The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

12.8.1.2. All ions present in the standard mass spectra at a relative intensity greater than 30% (most abundant ion in the spectrum equals 100 %) must be present in the sample spectrum. The relative intensities of ions must agree within ± 20% 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 30 and 70 percent.

12.8.1.3. Structural isomers not resolved 75% or greater must be reported as isomeric pairs e.g. xylenes, m&p.

12.8.2. For samples containing components not associated with the calibration standards, a library search using the most recent NIST/EPA Library may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

12.8.2.1. Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

12.8.2.2. The relative intensities of the major ions should agree within ± 20%.

12.8.2.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.8.2.4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

12.8.2.5. 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.

12.8.2.6. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

12.9. Quantitative Analysis: When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used should be the one nearest the retention time of that of a given analyte or as specified in the method. See Section 14 for calculations.

13. QUALITY CONTROL

13.1. Table 13.1 Quality Control

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per 20 samples	Target analytes must be less than ½ reporting limit. If results are reported to MDL, target analytes in MB should be non-detect	Re-analyze associated samples. ***Exceptions:*** If sample ND, report sample without qualification; If sample result >10x MB detects, report sample as not impacted by the blank contamination; If sample result <10x MB detects, and sample cannot be reanalyzed report sample with appropriate qualifier. Client must be alerted and authorize this condition.
Laboratory Control Sample (LCS)	DI water spiked with all target compounds; this is the same as the CCV and is to follow the CCV criteria	One per 20 samples	%Rec: 70-130% for all analytes %Diff ≤ 20%	Check spike solution and remake accordingly. Perform system maintenance determined necessary and reanalyze one time. As this is the CCV only two tries are allowed before recalibration is required. ***Exceptions:*** If LCS recovery is > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers. Or if insufficient sample is available, notify the project manager and qualify the data accordingly.

Matrix Spike (MS)	Client sample spiked with all target compounds	Upon client request, this is not method specified	%Rec: 70-130% for all analytes	If LCS and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences. Report the data appropriately qualified. For Minnesota Admin Contract Clients – all MS/MSD failures reanalysis of the MS/MSD and the original sample. If it is still out of control, investigate and document the cause in the associated narrative as well as qualifying appropriately.
MSD / Duplicate	MS Duplicate *OR* *(alternative)* Sample Dup	Upon client request.	%Diff ≤ 20%	Report results with an appropriate footnote.
Internal Standard	Labeled compounds	Added to all samples, batch QC and instrument QC	Internal standard areas must be ± 30% from the CCV or ± 50% and retention times must be within 30 seconds compared to the most recent ICAL.	If these criteria are not met, check system parameters, identify and correct likely causes, and re-run the samples. If the IS results appear out of control due to sample matrix, re-run the sample to confirm the matrix interference. Internal standard recoveries out low (high bias) – if compounds associated with the internal standard(s) that are outside the control limits are non-detect, the sample can be reported without re-analysis, however, if the outlier is not indicative of a system drift (i.e. If only one sample has internal standard drift, which is dissimilar from other samples around the injection time), re-analysis should be performed to rule out matrix effects. Internal standard recoveries out high (low bias) – re-analysis should be performed assuming there is sufficient sample volume remaining. Appropriate footnoting practices are also observed
Surrogate	Labeled compounds	Added to all samples, batch QC and instrument QC	%Rec: 75-125%	If these criteria are not met, check system parameters, identify and correct likely causes, and re-run the samples. If recoveries appear out of control due to sample matrix, re-run the samples to confirm the matrix interference and report the results with an appropriate footnote

14. DATA ANALYSIS AND CALCULATIONS

14.1. The RF is calculated as follows:

$$RF = \frac{A_x C_{is}}{A_{is} C_x}$$

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_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L)

14.2. Sample concentration of each analyte

$$\text{Concentration(mg/L)} = \frac{(A_x)(I_s)(DF)}{(A_{is})(RRF)}$$

Where: $\mathbf{A_x}$ = Area of characteristic ion for compound being measured.
$\mathbf{I_s}$ = Amount of internal standard injected (mg/L).
$\mathbf{A_{is}}$ = Area of characteristic ion for the internal standard.
RRF = Average Relative Response factor for compound being measured.
DF = Dilution Factor

14.3. See the Quality Manual for all other equations.

15. DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

15.1. See tables in section 11 & 13.

16. CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

16.1. See tables in section 11 & 13.

17. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

17.1. If not specifically listed in the tables in section 11 & 13, the contingencies are as follows. If there is no additional sample volume to perform re-analyses, all data will be reported as final with applicable qualifiers. If necessary, an official case narrative will be prepared by the Quality Manager or Project Manager.

18. METHOD PERFORMANCE

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually (per the method) per S-MN-Q-269, Method Detection Limit Studies for each matrix per instrument.

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-ALL-Q-020, Training Procedures.

18.3.1. Each analyst will analyze 4 repetitions at 2-5 µg/L. The initial demonstration of capability will be accepted if the averages of the amount recovered are within 80 – 120% accuracy and <20% precision. See SOP All-Q-020 for more information on performing IDC/CDCs.

18.3.2. At least quarterly analyze a quality control sample (QCS) from an external source. If the measured analyte concentrations are not of acceptable accuracy (70-130%), check the entire analytical procedure to locate and correct the problem.

18.4. **Periodic performance evaluation (PE)** samples are analyzed to demonstrate continuing competence per SOP S-MN-Q-258 (or equivalent replacement). Results are stored in the QA office.

19. METHOD MODIFICATIONS

19.1. The method uses procedural standards; the analysis of the LCS may be used as the calibration check standard.

19.2. EPA Method 524.3 Section 7.3.1 allows the flexibility in the concentration utilized for BFB. The lab is using 50 ng based on the shared systems with EPA 8260B and 624 methods which also use 50 ng or less for the daily tune concentration.

20. INSTRUMENT/EQUIPMENT MAINTENANCE

20.1. Please refer to the GC/MS 6890 instrument manual for maintenance procedures performed by the lab.

20.2. All maintenance activities are listed daily in maintenance logs that are assigned to each separate instrument.

21. TROUBLESHOOTING

21.1 2,2-Dichloropropane will degrade at room temperature and if an ending CCV/LCSD is ran at the end of the 12 hour tune window it is not uncommon to fail low for this analyte.

21.2 The purge and trap concentrator must be leak free in order to ensure properly sample purge efficiency and desorbion. If analyst notices significant decrease in response and suspects a possible leak, one can leak check the concentrator to ensure the p&t concentrator is free for leaks. This can be done through the software or manually by capping the vent valve of the concentrator and purging a blank.

22. SAFETY

22.1. **Standards and Reagents**: The toxicity and carcinogenicity of standards and reagents used in this method have not been fully defined. Each chemical compound should be treated as a potential health hazard. Reduce exposure by the use of gloves, lab coats and safety glasses. Material Safety Data Sheets (MSDSs) are on file in the laboratory and available to all personnel. Standard solutions should be prepared in a hood whenever possible.

22.2. **Samples**: Take precautions when handling samples. Samples should always be treated as potentially hazardous "unknowns". The use of personal protective equipment (gloves, lab coats and safety glasses) is required when handling samples. In the event a sample container must be opened, it is recommended to perform this in a hood whenever possible.

23. WASTE MANAGEMENT

23.1. Procedures for handling waste generated during this analysis are addressed in S-MN-S-003, Waste Handling.

23.2. In order to minimize the amount of waste generated during this procedure, analyst should prepare reagents in an amount which may be used in a reasonable amount of time (e.g., before a reagent expires).

24. POLLUTION PREVENTION

24.1. The company wide Chemical Hygiene and Safety Manual contains information on pollution prevention.

25. REFERENCES

25.1. Pace Quality Assurance Manual- most current version.

25.2. National Environmental Laboratory Accreditation Conference (NELAC), Chapter 5, "Quality Systems"- most current version.

25.3. The NELAC Institute (TNI); Volume 1, Module 2, "Quality Systems"- most current version.

25.4. "Method 524.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Rev. 4.1" Alford-Stevens, A., Eichelberger, J.W., Buddle, W.L.,

Slater, Jr., R.W., Munch, J.W., Bellar, T.A., Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, August 1992.

25.5. USEPA, SW-846, Method 8260B, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 2, December 1996.

25.6. "Method 524.3 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Rev. 1.0" Technical Support Center Office of Ground Water and Drinking water, U.S. Environmental Protection Agency, Cincinnati, Ohio, June 2009.

26. TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

26.1. Attachment I: Method 524.2 Target Analyte List, PRL, Characteristic Mass(m/z), and associated IS for Restek VMS- Rtx Column.

26.2. Attachment II: Common Dilution Factors for Waters.

27. REVISIONS

Document Number	Reason for Change	Date
S-MN-O-546-rev.12	Updated to LLC throughout document Table 11.1 – Modified parameter/frequency section for CCV	08Mar2017

ATTACHMENT I: Method 524.2 Target Analyte List, PRL, Characteristic Mass(m/z), and associated IS for Restek VMS- Rtx Column

Analyte	CAS Number	524.2 Waters (µg/L)	Primary Ion	Secondary Ion(s)	Internal Standard used for Quantitation
Dichlorodifluoromethane	156-59-2	1	85	87	2
Chloromethane	74-87-3	4	50	52	1
Vinyl Chloride	75-01-4	0.4	62	64	2
Bromomethane	74-83-9	4	94	96	2
Chloroethane	75-00-3	1	64	66	2
Trichlorofluoromethane	75-69-4	0.5	101	103	2
Dichlorofluoromethane	75-43-4	1	67	69	2
*Diethyl Ether	60-29-7	4	74	45, 59	2
1,1-Dichloroethene	75-35-4	0.5	96	61, 63	2
*Carbon Disulfide	75-15-0	1	76	78	2
Trichlorotrifluoroethane	76-13-1	1	151	101, 103	2
Iodomethane	74-88-4	4	142	127,141	2
*Allyl Chloride	107-05-1	4	76	41,39	2
Acetone d6 (IS#1)	666-52-4	IS	IS	46,64	
Methylene Chloride	75-09-2	4	84	86	2
*Acetone	67-64-1	20	58	43	1
trans-1,2-Dichloroethene	156-60-5	0.5	96	61,98	2
*Methyl-tert-butyl Ether	1634-04-4	0.5	87	57	2
1,1-Dichloroethane	75-34-3	0.5	63	65, 83	2
*Acrylonitrile	107-13-1	10	53	52,51	2
cis-1,2-Dichloroethene	156-59-2	0.5	96	61,98	2
2,2-Dichloropropane	594-20-7	1	77	97	2
Bromochloromethane	74-97-5	1	128	49, 130	2
Chloroform	67-66-3	0.5	83	85	2
Carbon Tetrachloride	56-23-5	1	117	119	2
*Tetrahydrofuran	109-99-9	10	71	72,42	2
1,1,1-Trichloroethane	71-55-6	0.5	97	99,61	2
Dibromofluoromethane (S)	1868-53-7	SS	113		2
*1,1-Dichloropropene	563-58-6	0.5	75	110,77	2
*2-Butanone (MEK)	78-93-3	5	43	72	2
Benzene	71-43-2	0.5	78	77	2
*Propionitrile	107-12-0	40	54	55,52	2
*Methacrylonitrile	126-98-7	4	41	67,39	2

ATTACHMENT I: Method 524.2 Target Analyte List, PRL, Characteristic Mass(m/z), and associated IS for Restek VMS- Rtx Column (Continued)

Analyte	CAS Number	524.2 Waters (µg/L)	Primary Ion	Secondary Ion(s)	Internal Standard used for Quantitation
Pentafluorobenzene (IS#2)	363-72-4	IS	168		
1,2 Dichloroethane d4 (S)	17060-07-0	SS	65	67,51	2
1,2-Dichloroethane	107-06-2	0.5	62	98	2
Trichloroethene	79-01-6	0.5	130	95, 132	3
1,4 Difluorobenzene (IS #3)	540-36-3	IS	114		
Dibromomethane	74-95-3	0.5	93	95,174	3
1,2-Dichloropropane	78-87-5	4	63	112	3
Bromodichloromethane	75-27-4	0.5	83	85,127	3
*Methyl Methacrylate	80-62-6	5	69	41,100	3
*cis-1,3-Dichloropropene	10061-01-5	0.5	75	77, 39	3
Toluene d8 (S)	2037-26-5	SS	98	100	4
Toluene	108-88-3	0.5	92	91	4
2-Nitropropane	79-46-9	10	43	41, 39	4
Tetrachloroethene	127-18-4	0.5	166	168, 129	4
*4-Methyl-2-Pentanone (MIBK)	108-10-1	5	43	58, 85	4
*trans-1,3-Dichloropropene	10061-02-6	0.5	75	77,39	4
1,1,2-Trichloroethane	79-00-5	0.5	83	97, 85	4
*Ethyl Methacrylate	97-63-2	4	69	41,99	4
Dibromochloromethane	124-48-1	0.5	128	127	4
1,3-Dichloropropane	142-28-9	0.5	76	78	4
1,2-Dibromoethane	106-93-4	0.5	107	109, 188	4
*2-Hexanone	591-78-6	5	43	58, 57	4
Chlorobenzene d5 (IS#4)	3114-55-4	IS	117		
Chlorobenzene	108-90-7	0.5	112	77, 114	4
Ethylbenzene	100-41-4	0.5	91	106	4
1,1,1,2-Tetrachloroethane	630-26-6	0.5	131	133, 119	4
m,p-Xylene	7816-60-0	1	106	91	4
o-Xylene	95-47-6	0.5	106	91	4
Bromoform	75-25-2	4	173	175,254	4
Styrene	100-42-5	0.5	104	78	4
Isopropyl benzene (Cumene)	98-82-8	0.5	105	120	4
4-Bromofluorobenzene (BFB) (S)	460-00-4	SS	95		5

ATTACHMENT I: Method 524.2 Target Analyte List, PRL, Characteristic Mass(m/z), and associated IS for Restek VMS- Rtx Column (Continued)

Analyte	CAS Number	524.2 Waters (µg/L)	Primary Ion	Secondary Ion(s)	Internal Standard used for Quantitation
Bromobenzene	108-86-1	0.5	156	77,158	5
Cis-1,4-Dichloro-2-butene	1476-11-5	4	53	77, 75	5
n-Propylbenzene	103-65-1	0.5	91	120	5
1,1,2,2-Tetrachloroethane	79-34-5	0.5	83	131, 85	5
2-Chlorotoluene	95-49-8	0.5	91	126	5
1,2,3-Trichloropropane	96-18-4	4	110	75, 77	5
1,3,5-Trimethylbenzene	108-67-8	0.5	105	120	5
*Trans-1,4-Dichloro-2-butene	110-57-6	10	53	88, 75	5
4-Chlorotoluene	106-43-4	0.5	91	126	5
tert-Butylbenzene	98-06-6	0.5	119	91,134	5
1,2,4-Trimethylbenzene	95-63-6	0.5	105	120	5
sec-Butylbenzene	135-98-8	0.5	105	134	5
p-Isopropyltoluene	99-87-6	0.5	119	134, 91	5
1,3-Dichlorobenzene	541-73-1	0.5	146	111, 148	5
1,4-Dichlorobenzene-d4 (IS#5)	3855-82-0	IS	152		
1,4-Dichlorobenzene	106-46-7	0.5	146	111, 148	5
n-Butylbenzene	104-51-8	0.5	91	92, 134	5
1,2-Dichlorobenzene	95-50-1	0.5	146	111, 148	5
1,2-Dibromo-3-chloropropane	96-12-8	4	75	155,157	5
Hexachloro-1,3-butadiene	87-68-3	1	225	227,223	5
1,2,4-Trichlorobenzene	120-82-1	0.5	180	182, 145	5
Naphthalene	91-20-3	1	128		5
1,2,3-Trichlorobenzene	87-61-6	0.5	180	182, 145	5
Total Trihalomethanes		4			
Xylene (total)	1330-20-7	1.5			3

The Reporting Limit for 524.2 water may be achieved by purging 10 mL of water instead of 5mL of water.

NOTE: Due to low area counts for the primary ions for analytes, 2-Butanone and 4-Methyl-2-Pentanone, Mass 43 is used as the quantitation ion and Acetone uses 58. The qualifying ions are Mass 43 for Acetone, Mass 72 for 2-Butanone and Mass 58 for 4-Methyl-2-Pentanone.

NOTE: Reporting Limits may vary. For the most current reporting limits, refer to LIMS system

ATTACHMENT II: COMMON DILUTION FACTORS FOR WATER SAMPLES

Water Dilution Factors		
Dilution	**Into 50 mL**	**Into 100 mL**
2x	25 mL	n/a
5x	10 mL	20 mL
10x	5 mL	10 mL
20x	2.5 mL	5 mL
25x	2 mL	4 mL
50x	1000 uL	2 mL
100x	500 uL	1000 uL
200x	250 uL	500 uL
500x	100 uL	200 uL
1000x	50 uL	100 uL
10000x	5 uL	10 uL

APPENDIX B

GF SOPS

NATIONAL PRESTO INDUSTRIES

SOP 1 - GROUNDWATER SAMPLING AND EQUIPMENT DECONTAMINATION

Field Equipment and Materials List

The field equipment and materials needed to collect groundwater samples from monitoring wells are summarized by method in the following table.

Field Equipment/Material Description	Sample Method		
	PDB (1)	Bailer	Pump
Well lock key	X	X	X
Electronic water level indicator	X	X	X
Disposable gloves, paper towels, and potable water in spray bottles	X	X	X
Potable water/Alconox detergent solution in spray bottles for decontamination	X	X	X
PDB and HydraSleeve® supplies (to deploy for next sampling round) (2)	X	X	X
Peristaltic pump, tubing, and supplies to field filter samples for cadmium (3)	X	X	X
Disposable bailers and rope		X	
Submersible pump			X
Portable electric generator for pump (or power supply from field vehicle)			X

FOOTNOTES:
(1) PDB = passive diffusion bag or HydraSleeve® if sample will be analyzed for cadmium (Cd).
(2) Supplies include carboy with distilled water to fill PDB at well before deployment.
(3) Supplies include single-use mason jar and 0.45-micro inline filter for each sample to be analyzed for Cd.

Pumped groundwater samples will be collected either from a sample tap or dip bucket and properly preserved in accordance with SOP 2. At locations where a dip bucket sampler is employed (e.g., manhole MH-18), the dip bucket sampler will be cleaned with paper towels, a potable water/Alconox solution, and potable rinse water before starting and between each use. The paper towels will be properly disposed of after each use.

Field Instrument Calibration

Before going into the field, the sampler will verify that the electronic instruments to be used are operating properly. Before sampling, field staff will calibrate each instrument prior to use according to the manufacturer's instructions and will record the calibration time and readings in the field log book or on the sample data sheet.

Field Equipment Decontamination

Before purging or sampling begins, all reusable field equipment (e.g., electronic water level indicator) will be cleaned with paper towels, a potable water/Alconox solution, and potable rinse water. The paper towels will be properly disposed of after each use.

Well Condition Assessment

The sampler will:

- Assess the condition of the steel protective pipe and locking cover (for wells completed above grade), flush-mount frame and lid (for wells completed below grade), surface pad, well casing, and cap
- Note any unusual conditions in the field log book or on the field data sheets.
- Remove the locking cover or locked cap to access the well.

Sampling Procedure and Decontamination Protocol

From the 1980s and into the mid-1990s, groundwater samples were collected from monitoring wells and piezometers at National Presto Industries (NPI) using the following procedure required by the U.S. Environmental Protection Agency (EPA) and Wisconsin Department of Natural Resources (WDNR). A minimum of ten casing and filter pack volumes of water was removed from each well prior to sampling. At the time, this was done using a PVC bailer. The bailer was then used to collect the sample, and a bottom-emptying device was used to minimize the loss of volatile compounds during the transfer of the sample to the sample container.

Starting in the late 1990s, Grundfos submersible pumps were used to purge and sample the wells instead. These pumps are capable of flows low enough for low-flow sampling, although they were not originally used that way. Bailers were still occasionally used to purge and sample those wells that had less than a foot or two of water in them due to low groundwater elevations in the aquifer.

Starting in March 2009, two relatively new technologies for collecting groundwater samples from monitoring wells were implemented over time. One was the use of passive diffusion bags (PDBs). Following a trial use of the bags, the EPA approved the routine use of PDBs in a May 20, 2009, letter. Since that time, PDBs have been used whenever possible for collecting groundwater samples for volatile organic compound (VOC) analyses at NPI. The second technology was the trial use of the HydraSleeve®, a no-purge sampler that is intended to be used to sample for dissolved cadmium (Cd), which is not compatible with a PDB. The trial test of the HydraSleeve® resulted in comparable concentrations for dissolved Cd and VOCs versus the traditional methods of sampling (i.e., bailing and pumping). On March 16, 2011, the EPA

approved the use of the HydraSleeve® when sampling for dissolved Cd or dissolved Cd and VOCs in NPI monitoring wells and piezometers. However:

- The option of using bailers and submersible pumps was retained for flexibility.
- The EPA and WDNR have both stated that, in accordance with the WDNR *Groundwater Sampling Field Manual* (PUBL-DG-038 96), removal of four well/casing volumes was adequate for purging wells at NPI. Consequently, when a bailer or submersible pump is used, only four casing volumes will be removed prior to sampling. The casing volume will be calculated using Equation 1 in the September 1996 WDNR field manual.

Descriptions of each sampling method follow.

Passive Diffusion Bags (PDBs)

PDBs are semi-permeable LDPE bags manufactured specifically for collecting groundwater samples for analysis of VOCs. The bags are ordered directly from the manufacturer, EON Products Inc. (EON). The manufacturer also provides custom-made, labeled, polyethylene tethers for each individual well, based on the depth of the well. The tethers are made based on the depth of each well, and each has two stainless-steel rings that allow the PDBs to be securely attached to the tether. PVC caps for hanging the tethers and stainless-steel weights to help hold the bags in place within the wells are also provided by the manufacturer.

NPI obtains distilled water in 55-gallon drums from a local vendor. Gannett Fleming, Inc. staff transfer distilled water from a drum into a dedicated 5-gallon carboy and use the water from the carboy to fill the individual PDBs at each well.

The PDBs are deployed at least two weeks prior to sampling to ensure adequate time for equilibration within the aquifer. The depth to water is measured in each well prior to setting the locations of the rings on the tether to ensure that the bag is located approximately in the middle of the saturated interval within the well at the time it is deployed.

Upon retrieval, the bag is punctured using a new one-time-use "straw," or the sample can be carefully and slowly poured from the fill port. The contents of the bag are transferred into laboratory-supplied, 40-ml vials containing hydrochloric acid preservative in accordance with SOP 2. The punctured PDB and sampling straw are disposed of after each use.

If the well is scheduled to be sampled within the next 12 months, a new PDB filled with distilled water will be attached to the tether, and it will be lowered back into the well. The vertical position of the PDB will be adjusted, as needed, so that it is located in the approximate middle of the saturated interval. The locking cover or cap will be reinstalled to secure the well. In the

event the existing PDB appears to be in good condition and is not punctured during the sampling process, then it may be reused instead of deploying a new PDB to conserve resources.

If the well is not scheduled to be sampled within the next 12 months, the tether and weight will be removed and wound around a dedicated plastic reel for cleaning and storage, and the locking cover or cap will be reinstalled to secure the well. The reel with looped tether and weight(s) will then be washed with a potable water/Alconox solution in one tub and double-rinsed using potable water in two separate tubs. The cleaned reel with looped tether and weight(s) will then be hung to air dry at NPI until they are next needed.

No-Purge Samplers (HydraSleeve®)

The HydraSleeve® is a collapsible tube of 4-mil polyethylene, 1.75" x 30" with a capacity of 650 ml and a check valve at the top. The HydraSleeve® is designed to collect a representative water sample from a monitoring well without purging. The HydraSleeve® is manufactured by GeoInsight of Las Cruces, New Mexico, and they are ordered from EON. EON provides custom-made labeled polyethylene tethers for each individual well, based on the sampling interval of the well. At the end of a rope, a stainless-steel spring is attached. The spring is to keep the top of the HydraSleeve® open. Near the top of the tube is a built-in check-valve. On the bottom of the HydraSleeve®, a stainless-steel weight is attached. In wells with little saturated screen length, a stainless-steel weight, called a top collar weight, is attached at the top of the tube. The top collar weight compresses the tube on the bottom of the well to maximize the volume of water recovered when the tube is retrieved. The bottoms of the PVC caps have a stainless-steel ring to which the HydraSleeve® tether is attached.

The HydraSleeve® samplers are used primarily to collect samples from wells for Cd analysis. The HydraSleeves® are deployed at least two weeks prior to sampling to ensure adequate equilibration within the aquifer. The depth of the water in the well is measured prior to setting the location of the HydraSleeve®.

The HydraSleeve® will be located 1 to 2 feet below the sampling zone. As the HydraSleeve® is pulled though the sample zone, water passes through the check-valve and into the tube. The HydraSleeve® should be full as it passes out of the sampling zone; and once full, the check-valve will not allow any more water to enter the tube. The HydraSleeve® will be retrieved at an approximate rate of 1 to 2 feet per second. In wells where the depth of water is less than 4 feet, the HydraSleeve® will be pulled up toward the top of the sampling interval and allowed to drop back to its original position in the well. The action will be repeated until the HydraSleeve® is filled. Once filled, the HydraSleeve® will gently be removed from the well; a small diameter plastic "straw" supplied with the HydraSleeve® will then be inserted near the bottom of the tube. The sample will then discharge from the HydraSleeve® through the straw and into laboratory-supplied sample containers and/or one-time-use glass jars used to temporarily hold

the sample until it is filtered (for Cd analysis) using either a hand-held vacuum pump and filter paper or peristaltic pump with a 0.45-micron, single-use inline filter. The sample will be pumped from its disposable glass jar through its disposable filter and directly into a sample container, supplied by the laboratory, that contains nitric acid for preservation in accordance with SOP 2. The HydraSleeve® and sampling straw will be disposed of after each use.

If the well is scheduled to be sampled within the next 12 months, a new HydraSleeve® will be attached to the tether and deployed into the well. The vertical position of the HydraSleeve® will be adjusted, as needed, so that it is located 1 to 2 feet below the sampling zone. The locking cover or cap will be reinstalled to secure the well.

If the well is not scheduled to be sampled within the next 12 months, the tether and weight will be removed and wound around a dedicated plastic reel for cleaning and storage, and the locking cover or cap will be reinstalled to secure the well. The reel with looped tether and weight(s) will then be washed with a potable water/Alconox solution in one tub and double-rinsed using potable water in two separate tubs. The cleaned reel with looped tether and weight(s) will then be hung to air dry at NPI until they are next needed.

Bailer

In the event that there is water in a well, but its depth is insufficient to use a submersible pump, HydraSleeve®, or PDB, a bailer will be used to purge the well and obtain a groundwater sample (this would likely occur when the depth of water in the well is less than 2 feet). A section of new polypropylene rope will be attached to a new one-time-use bailer. The bailer will be lowered into the well. At the water table, it will be lowered gently and slowly into the water to a point no closer than 4 to 6 inches from the bottom of the well. The bailer will then be raised to the surface slowly and gently to minimize disturbance of the water in the well casing. The appropriate purge volume will be determined in accordance with Equation 1 in the WDNR *Groundwater Sampling Field Manual* (PUBL-DG-038 96). The well will be purged of four casing volumes of water or until it is purged dry. The well will then be sampled (following recovery if bailed dry) and preserved in accordance with SOP 2. The rope and bailer will be disposed of after each use.

Submersible Pump (Low-Flow Purging/Sampling)

The purging will be done by lowering a decontaminated 2-inch submersible pump, or other pump capable of low-flow sampling, down the well casing to a point where the pump intake is about halfway between the water table surface and the bottom of the well. A closed flow-through cell will be attached to the discharge end of the pump. The pump will then be started and operated at a purge low-flow rate (less than 1L/min) and sample flow rate (less than 300ml/min) to ensure that air is not pulled into the pump causing turbulence in the water and to

ensure that there is little or no water level drawdown. A graduated container and stop watch will be used to determine the actual flow rate. A water level meter will be used to measure the depth to groundwater during pumping. The depth to water and flow rate will be monitored every two to five minutes or 0.5 well volumes and the results recorded on the field sheet.

A probe(s) capable of measuring conductivity, temperature, dissolved oxygen (DO), and pH will be placed in the closed flow-through cell. The conductivity, temperature, DO, and pH meter(s) will be calibrated in the field in accordance with the manufacturer's specifications. Conductivity, temperature, DO, and pH readings will be measured at the beginning and at approximately two- to five-minute or 0.5 well volumes intervals during the purging to confirm that the water being pumped has reached chemical equilibrium. The readings for conductivity, temperature, DO, and pH will be logged on the field data sheets. The last two conductivity readings should be plus or minus 5 umhos/cm for values < 1000 and plus or minus 10 umhos/cm for values > 1000. The pH should be plus or minus 0.1 standards units, and the temperature should be plus or minus 0.1 degree Celsius. The DO readings should be within 0.2 mg/L of each other. If these criteria are not met, the purging will continue until they are met or until the readings for each indicator parameter listed above vary within +/- 10 percent over three or more consecutive readings spaced approximately two minutes or approximately 0.5 well volumes or more apart.

Purging will be considered complete when the readings for all four of the field analytes have stabilized, as described above. Laboratory-supplied vials for VOCs or mason jars for Cd will then be slowly filled from the sampling hose located on the side of the pump frame and preserved in accordance with SOP 2.

After each well is purged and sampled, the pump, hose, and frame will be washed on the outside with a potable water/Alconox solution and double-rinsed using potable water. The inside of the pump and hose will be decontaminated using the same procedure. A rack of three 4-inch-diameter, Schedule 40 PVC tubes that are 4.5 feet long (3-gallon capacity each) has been constructed. The potable water/Alconox solution will be placed in the first tube, while potable water will be poured into the other two. The pump will be placed into the first tube and turned on, allowing the solution to cleanse the exterior of the pump and flow through the pump and hose. The pump discharge will be directed onto the exterior of the hose and frame to provide a detergent cleaning of that part of the equipment. The pump will then be placed in the second tube, which contains potable water for the initial rinse. After the potable water in the second tube is evacuated, the pump will be moved to the third tube, which also contains potable water for the second and final rinse. The discharge from the second and third tubes will also be directed onto the exterior of the hose and frame to rinse them. Finally, all three tubes will be thoroughly rinsed with potable water between each well.

NATIONAL PRESTO INDUSTRIES

SOP 2 – WATER AND AIR SAMPLE HANDLING AND QA/QC PROTOCOLS

Whenever water samples are collected for analysis of volatile organic compounds (VOCs) at National Presto Industries (NPI):

- One duplicate for NPI VOC analysis will be collected for every ten wells sampled.
- One matrix spike (MS) and one matrix spike duplicate (MSD) for NPI VOC analysis will be collected for every twenty wells sampled.
- One trip blank for NPI VOC analysis will be submitted in each cooler shipped to the lab.

Sample Preservation, Labeling and Shipping

All water samples for VOC analysis will be placed in laboratory-supplied, 40-mL vials containing hydrochloric acid (HCl). Two or three vials will be filled for each sample, depending on the available sample volume. This volume allows for internal QA/QC and dilutions by the laboratory, if necessary. Each vial will carefully be filled to minimize volatilization of any VOCs in the sample. A Teflon-lined cap will be placed on each of the sample vials, and the vials will be visually examined to ensure there are no air bubbles. Each vial will then be labeled and placed on ice prior to shipment to the laboratory. Water samples to be analyzed for dissolved cadmium (Cd) will be field-filtered using a 0.45-micron, single-use disposable filter and placed into laboratory-supplied, 250-mL plastic bottles containing nitric acid (HNO_3).

The method of sample delivery to the laboratory will be overnight courier for water samples; ground courier is acceptable for air samples. Each shipment of samples will be accompanied by a completed chain-of-custody (COC) record.

Gannett Fleming, Inc. (GF) will use its internal field data sheets and NPI or GF field book to manage sample collection and documentation. The COC forms will be used to track the samples from the field to check in at the laboratory. Field personnel will record pertinent data/information onto the field sheets, field book, sample labels, and COC records by hand, using a ballpoint pen, in the field. Sample labels and COC records are used to track samples from the field to the laboratory.

Chain-of-custody records will be signed in ink by the samplers and the individual relinquishing custody. GF will then follow the sample packaging and shipment procedures summarized below to ensure that the sample(s) arrive(s) at the laboratory with the COC intact.

1. Immediately after sample collection, sample containers will be labeled with the appropriate identifiers.
2. Water samples will be placed in plastic bubble bags or the cardboard vial containers and then in a cooler containing bags of ice and maintained at ≤6 degrees Celsius (°C). Air samples collected in Summa canisters will be returned to their initial shipping containers and will be kept at ambient temperature. The coolers and shipping containers will remain in a secured area or in view of the sampler until it is properly sealed for shipment to the laboratory.
3. Prior to shipping, the COC records and all other relevant documents will be completed and sealed in plastic bags inside the cooler or shipping container. Cushioning material, such as bubble-wrap, will be placed in the coolers and containers as needed to ensure safe transit of the samples to the laboratory.
4. A trip blank for NPI VOCs will be included in every cooler used to ship water samples to be analyzed for NPI VOCs.
5. The shipping cooler/container will then be sealed with tape in a manner that will indicate whether the cooler/container was opened.
6. The field sampler is personally responsible for the care and custody of the samples until they are transferred to other personnel or are properly dispatched to an overnight carrier or directly to a laboratory. When transferring possession of the samples, the individuals relinquishing and receiving the samples will sign, date, and note the time of transfer on the COC record. Commercial carriers are not required to sign off on the COC record as long as the record is sealed inside the sample cooler/shipping container.

Laboratory Analytical Methodology and QA/QC

All water samples will be analyzed by a Wisconsin-certified laboratory. The samples for VOC analysis from the monitoring wells, extraction wells, cascade aerators, and manhole MH-18 will be analyzed using EPA Method 8260B. The analyte list is a short list of the 8260 compounds and is based on the known contaminants at the site. The analytes consist of the following compounds:

- Trichloroeth(yl)ene (TCE)
- 1,1,1-Trichloroethane (TCA)
- Tetrachloroeth(yl)ene (PCE)
- 1,1-Dichloroethane (DCA)
- 1,1-Dichloroeth(yl)ene (DCE)

Samples collected from the water supply wells at the Eau Claire Municipal Well Field (ECMWF) will be analyzed for the same VOCs using Method 524.2, per the federal Safe Drinking Water Act.

Air samples will be analyzed by a NELAC-certified laboratory for VOCs using Method TO-15. Air samples (of the exhaust gas from the Melby Road Disposal Site [MRDS] and main building soil vapor extraction [SVE] systems) will be analyzed for TCE; 1,1,1-TCA; PCE; and 1,1-DCA. Exhaust gas samples from the MW-34/70 area SVE system will be analyzed for TCE.

Annual water samples from MH-18 will also be analyzed for hardness (as $CaCO_3$) by EPA Method 2340B, polycyclic aromatic hydrocarbons (PAHs) by EPA Method 8270, hexavalent chromium by Standard Method 3500-Cr B, and dissolved metals by EPA Method 6010. The laboratory provides a Level 3 Contract-Laboratory-Program-like QA/QC data package with its water sample reports.

The laboratory sample custodian will receive all incoming samples and indicate receipt by signing the accompanying custody records and retaining copies of the signed COC records as permanent records. The laboratory sample custodian will record all pertinent information concerning the sample, including the persons delivering and receiving the sample, the date and time received, the method by which the sample was transmitted to the laboratory, the sample condition at the time of receipt (sealed, unsealed, or broken container; temperature; or other relevant remarks), the sample identification number, and any unique laboratory identification number associated with the sample. This information should be entered into a computerized laboratory information management system (LIMS).

The laboratory will provide a secure storage area, restricted to authorized personnel, for all samples. Laboratory analytical personnel are responsible for the care and custody of the sample upon receipt and during the required analyses.

At the completion of water sample analysis, any unused portion of the water sample, together with all identifying labels, will be returned to the appropriate storage location. The returned tagged sample will be retained in storage for 30 days from the date the final laboratory report is issued. Unless otherwise requested by GF, the samples will then be disposed of in accordance with the laboratory's protocol. Air samples will be disposed of following analysis.

When the laboratory receives a sample shipment, its LIMS will generate the in-house identification numbers in accordance with its sample receipt and COC SOP.

Data Validation

Mary Wehbe of MCW Scientific Solutions, Cedar Park, Texas, will perform data validation for the water samples collected at the NPI site. See QAPP Worksheet #36 in Section 4.0 of the QAPP for details.

AIR CANISTERS

Instructions for Canister Grab Sampling

(Tools needed: one ended 9/16" wrench)

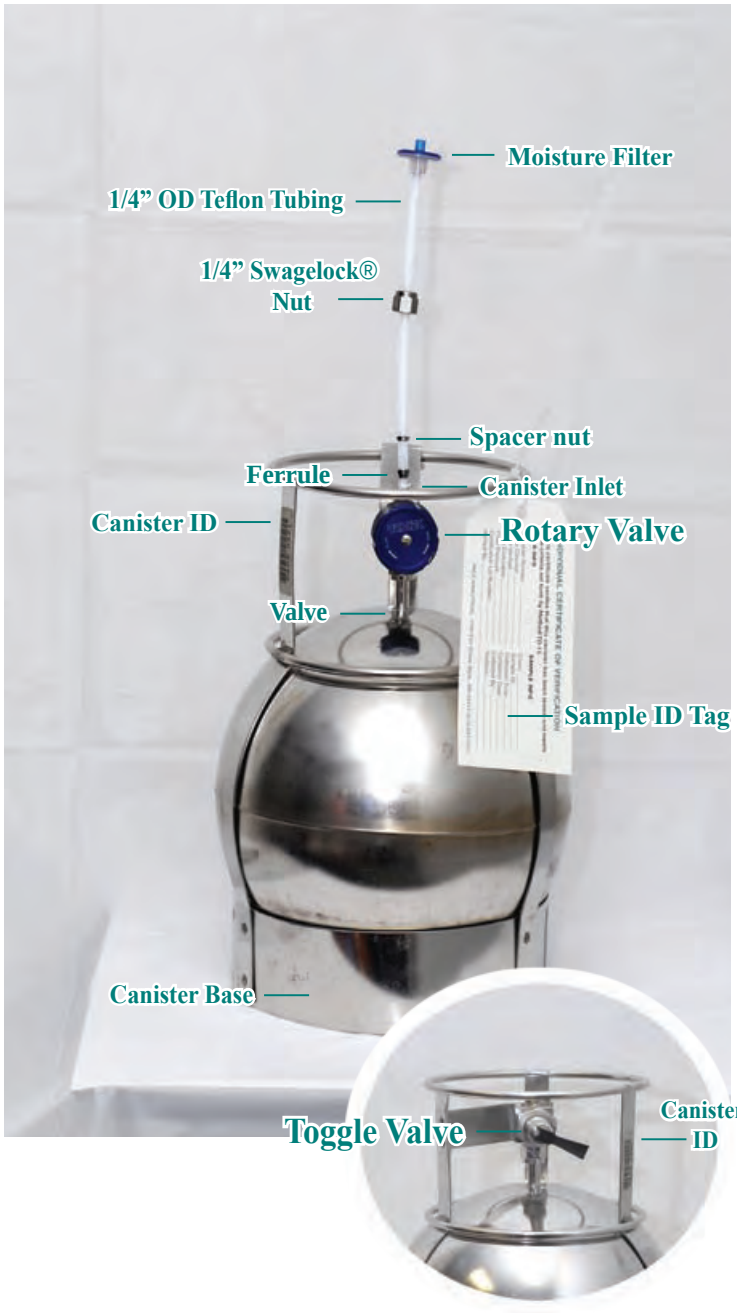
1. INSPECTION – Inspect your canister shipment upon arrival. Compare the contents with the packing slip and notify Pace Analytical of any discrepancy or damage. Familiarize yourself with the contents you received by comparing them to the pictures on the right. Do not open the valve until you are ready to sample. Even a small loss of vacuum will compromise your sample.

2. CONNECTION – Remove the brass cap from the top of the can with a 9/16" wrench. If you are connecting to a predetermined sampling point you may have received the following: 6 inches of ¼ inch OD Teflon tubing, ¼ inch Swagelock® nut, ferrule, spacer nut and moisture filter (if requested). Connect these items in series using the pictures on the right as a guide. The spacer fits between the nut and the ferrule. The ferrule must be pointed down toward the canister. Please note the connection to the canisters utilizes Swagelock® threading. For a proper connection, it's important that no cross-threading occurs. The canister connection is made by hand-tightening the Swagelock® nut. Once connected, use an open ended (9/16") wrench to further tighten the connection. Make sure that the connection is firmly tightened. The final connection must be leak tight recognizing also that over-tightening can cause leaks as well. Do not use pliers or adjustable-end wrenches to tighten this Swagelock® connection. Use only open ended wrenches for tightening. The canister is now ready for sampling.

3. SAMPLING – To begin sampling simply open the canister valve (you may have either a rotary valve or a toggle valve). One full turn counter clockwise for the rotary valve is sufficient. The toggle valve will open by flipping upward. During the initial sampling process you will hear a rush of air. Without a flow restriction the canister will fill in approximately 30-45 seconds.

4. COMPLETION – After sampling is complete, close the canister valve. Disassemble the components and return them in the original shipping package they were received in. Verify the contents for return to the laboratory. Complete the Chain-of-Custody form and return with the samples to the laboratory. Be sure to reference the canister ID on the Chain-of-Custody.

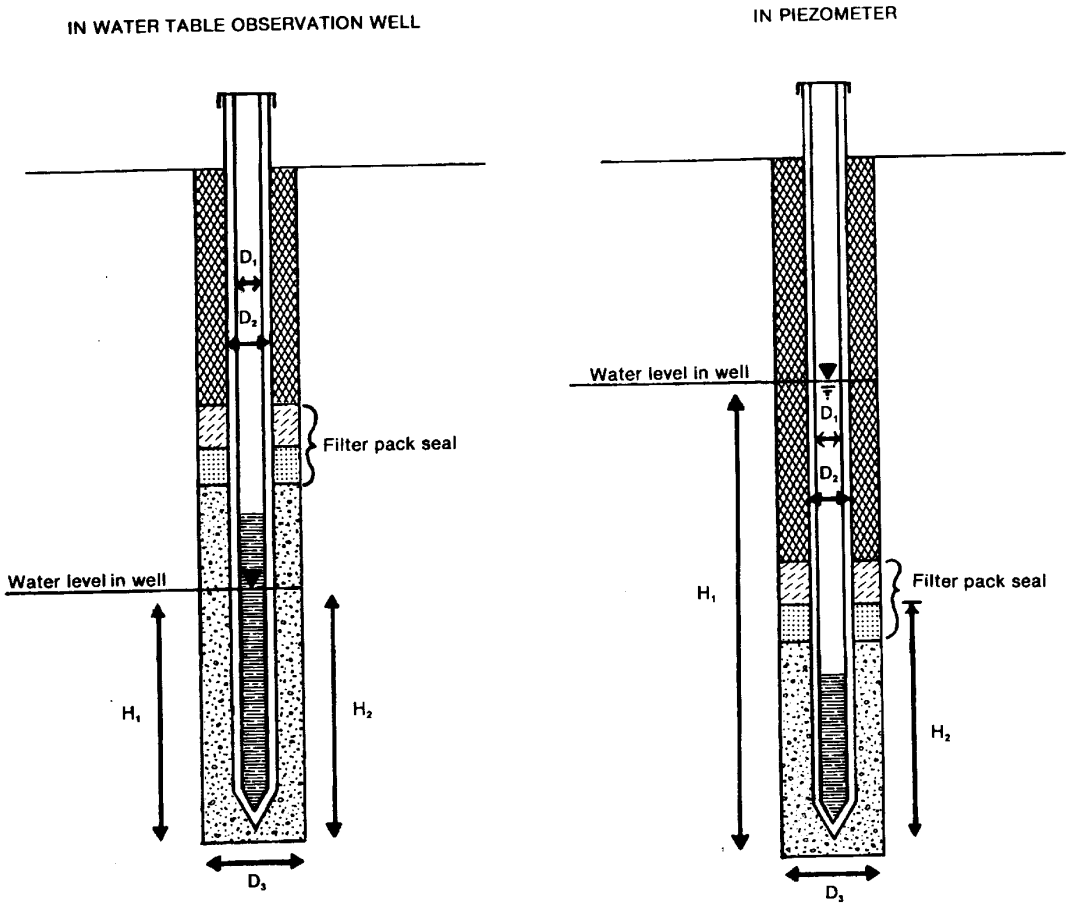
Grab Sample Configuration



Questions? Please call the Air Technical phone number 612-607-6386

SOP 4 - WELL ABANDONMENT (see Section NR 141.25 below)

CALCULATION OF WELL VOLUME



(2) WELLS THAT CAN BE PURGED DRY. All permanent groundwater monitoring wells that can be purged dry shall be developed in a manner which limits agitation by slowly purging the well dry. Wells which can be purged dry may not be surged and no water may be added to the well.

History: Cr. Register, January, 1990, No. 409, eff. 2−1−90; am. (intro.), (1) (a) and (b) and (2), Register, June, 1991, No. 426, eff. 7−1−91.

NR 141.23 Well and borehole construction documentation. (1) All permanent groundwater monitoring well construction shall be reported to the department, using forms and instructions provided by the department, within 60 days after the well has been installed. The completed report shall include the following information:

(a) Well location,

(b) Well casing material and installation procedures,

(c) Well screen materials and installation procedures,

(d) Filter pack materials and installation procedures,

(e) Sealing materials and installation procedures,

(f) Drilling methods and fluids used for installation,

(g) Borehole diameter,

(h) Well development procedures,

(i) Sieve analysis, and

(j) Any other information deemed necessary by the department.

(2) All permanent groundwater monitoring wells installed after February 1, 1990 shall be labeled with labels supplied by the department.

(3) All borehole construction data shall be reported to the department using forms and instructions supplied by the department within 60 days after construction. The completed report shall include the following data: the results of any soil tests done and a description of the soil structure, soil color, mottling, moisture content, layering, jointing, lenses, fractures, organic matter and voids and any other information deemed necessary by the department. The constructor shall report any decontamination procedures used between borehole installations.

History: Cr. Register, January, 1990, No. 409, eff. 2−1−90; am. (1) (h), renum. (1) (i) to (j), cr. (1) (i), Register, June, 1991, No. 426, eff. 7−1−91.

NR 141.25 Abandonment requirements. The following requirements apply to the abandonment of all boreholes greater than 10 feet deep or which intersect a water table and all groundwater monitoring wells. The department may require, by order or other appropriate means, that any borehole or monitoring well be abandoned. The department shall consider the following factors in determining whether a borehole or monitoring well should be abandoned: purpose, location, groundwater quality, age and condition of the well or borehole potential for groundwater contamination and well or borehole construction.

(1) TIMELINES FOR ABANDONMENT. (a) A borehole shall be abandoned within 3 working days after its use has been discontinued.

(b) Any permanent groundwater monitoring well no longer being used to gather information on geologic or groundwater properties shall be abandoned within 60 days after its use has been discontinued.

(c) Any groundwater monitoring well found by the department to be acting as a conduit for groundwater contamination shall be abandoned within 15 working days after written notification by the department.

(d) Any groundwater monitoring well constructed after February 1, 1990 not meeting the requirements of this chapter shall be abandoned and replaced with a monitoring well meeting the requirements of this chapter or any department approval granted under this chapter within 60 days after installation of the noncomplying well or 15 days after written notification by the department that the well is noncomplying.

(2) ABANDONMENT PROCEDURES. (a) *Boreholes.* Any borehole intersecting the water table or greater than 10 feet deep, whose use has been discontinued, shall be abandoned according to the requirements of par. (d).

(b) *Monitoring wells — impermeable annular space seals.* A permanent groundwater monitoring well known to be constructed with an impermeable annular space seal shall be abandoned according to the requirements of par. (d) after the protective cover pipe and ground surface seal have been removed and the well casing cut off at least 30 inches below the ground surface. The well casing may be completely removed during abandonment by pulling the well casing, overdrilling around the casing and then pulling the well casing out of the ground or by drilling out the well casing completely. If the well casing is to be removed, the well shall be sealed as the casing is removed.

(c) *Monitoring wells — permeable annular space seals and wells in waste areas.* A groundwater monitoring well not known to be constructed with an impermeable annular space seal or located in an existing or planned future waste disposal or treatment area shall be abandoned by removing the protective cover pipe and the ground surface seal and then completely removing the well casing. The well casing shall be pulled out of the ground as the well is filled according to the requirements of par. (d).

(d) *Sealing requirements.* Boreholes and groundwater monitoring wells shall be abandoned by complete filling with neat cement grout, bentonite−cement grout, sand−cement grout, concrete or bentonite−sand slurry. When a tremie pipe is used to place the sealing material, the procedures of s. NR 141.10 (2) shall be followed. A tremie pipe shall be used to abandon groundwater wells and boreholes greater than 30 feet in depth or with standing water. Groundwater monitoring wells and boreholes greater than 100 feet in depth shall be sealed with a tremie pipe−pumped method. Bentonite may be used as a sealing material without the use of a tremie pipe under the following conditions:

1. Bentonite granules may be used for abandonment of boreholes and groundwater monitoring wells less than 25 feet deep and when there is no standing water above the filter pack seal.

2. Bentonite chips no greater than 3/8 inch in diameter or bentonite pellets may be used for abandonment of boreholes and groundwater monitoring wells less than 50 feet deep and the depth of standing water is less than 30 feet.

3. Bentonite chips no greater than 3/8 inch in diameter or bentonite pellets may be used for abandonment of boreholes and groundwater monitoring wells which are greater than 4 inches in diameter and less than 250 feet deep and the depth of standing water is less than 150 feet.

(3) SEALANT SETTLEMENT. Any settling of the sealant material shall be topped off. Sealing material may be terminated 30 inches below the ground surface in agricultural areas to avoid interference with agricultural activities. A native soil plug shall be placed on top of the settled sealing material in such cases.

(4) ABANDONMENT DOCUMENTATION. All borehole and permanent groundwater monitoring well abandonments shall be reported to the department within 60 days of the abandonment on forms supplied by the department. In addition to the information required on the form, the person performing the abandonment shall report any decontamination procedures used between borehole and well abandonments.

History: Cr. Register, January, 1990, No. 409, eff. 2−1−90; am. (2) (b), (2) (d) 1. to 3. and (3), Register, June, 1991, No. 426, eff. 7−1−91.

NR 141.27 Driven point wells. Driven point wells with galvanized steel drive pipes and contaminant compatible well screens may be used as permanent groundwater monitoring wells if prior department approval is obtained. Written documentation shall be supplied to the department prior to installation indicating:

(1) That the well is to be used only for water table elevation measurements or to monitor for parameters for which the well casing and screen material will not interfere with the analytical results;

(2) That the well will not provide a conduit for contaminants to enter the groundwater; and

(3) That information on subsurface stratigraphy is not needed. In situations where subsurface geologic information is needed, a separate borehole shall be constructed to collect the required data.

History: Cr. Register, January, 1990, No. 409, eff. 2−1−90.

NR 141.29 Temporary groundwater monitoring wells. Temporary groundwater monitoring wells may be installed according to less stringent standards than specified for permanent groundwater monitoring wells. Any temporary monitoring well construction shall be approved by the department prior to its installation. All temporary monitoring wells shall be abandoned in accordance with s. NR 141.25 within 120 days after their installation.

History: Cr. Register, January, 1990, No. 409, eff. 2−1−90.

NR 141.31 Special circumstances and exceptions. **(1)** The department may require or approve more restrictive or alternative well material, assembly, installation, development or abandonment if the contaminant concentrations or geologic setting require alternative construction. Prior written approval is required before any alternative materials are used in monitoring well installation.

(2) Exceptions to the requirements of this chapter may be approved by the department prior to installation or abandonment. An exception request shall state the reasons why compliance with the rule requirements is infeasible. The department may conditionally approve an exception by requiring materials or procedures which safeguard against contamination and result in groundwater monitoring well construction which is substantially equivalent to the requirements of this chapter. Failure to comply with the conditions of an exception voids the department's approval of the exception.

History: Cr. Register, January, 1990, No. 409, eff. 2−1−90.

The first page of and Figure 1 from Chapter NR 141 follow for reference.

Chapter NR 141

GROUNDWATER MONITORING WELL REQUIREMENTS

NR 141.01 Purpose. The purpose of this chapter is to establish minimum acceptable standards for the design, installation, construction, abandonment and documentation of groundwater monitoring wells. These rules are adopted under chs. 281, 160 and 227, Stats.

History: Cr. Register, January, 1990, No. 409, eff. 2−1−90; correction made under s. 13.93 (2m) (b) 7., Stats., Register, March, 2000, No. 531.

NR 141.03 Applicability. This chapter applies to all persons installing and abandoning groundwater monitoring wells and boreholes for purposes regulated by the department under ch. 160, 281, 283, 289, 291, 292, 293 or 299, Stats., or in permits, plan approvals, licenses or orders issued under those chapters. In addition, this chapter applies to all persons installing groundwater monitoring wells and boreholes in fulfillment of terms of a contract with the department. All wells and boreholes installed for purposes regulated by the department under this chapter shall be abandoned according to s. NR 141.25. All other wells and boreholes shall be abandoned according to the provisions of ch. NR 812.

Note: Additional requirements concerning soil testing and groundwater sampling are located in other chapters regulating wastewater and solid and hazardous waste disposal, see chs. NR 110, 206, 213, 214, 508, 512 and the 600 and 700 series.

History: Cr. Register, January, 1990, No. 409, eff. 2−1−90; am. Register, June, 1991, No. 426, eff. 7−1−91; correction made under s. 13.93 (2m) (b) 7., Stats., Register, September, 1995, No. 477; corrections made under s. 13.93 (2m) (b) 7., Stats., Register, March, 2000, No. 531.

NR 141.05 Definitions. In this chapter:

(1) "Air rotary drilling" means a drilling method whereby the borehole is advanced using a circular rotating action applied to a string of drilling rods which have a diffused discharge bit attached to the bottom of the rods. Pressurized air is forced through the drilling rods and cools the drilling tools and removes the cuttings from the borehole.

(2) "Annular space seal" means the following:

(a) For wells constructed with filter packs, it is the material placed above the top of the filter pack or the filter pack seal up to the surface seal and between the well casing and the adjacent formation; or

(b) For wells constructed into bedrock formations and without well screens, it is the material placed from the bottom of the enlarged borehole up to the surface seal, between the well casing and the adjacent formation.

(2m) "Aquifer test well" means a well installed to provide information on the hydraulic conductivity, transmissivity, storage coefficient, capture zone, specific capacity, radius of influence or other physical parameters of an aquifer, defined geologic unit, or water bearing formation through the imposition of a sustained stress on the aquifer by removal of water.

(3) "ASTM" means american society for testing and materials.

(5) "Bedrock" means the solid rock underlying any loose surficial material such as soil, alluvium or glacial drift. Bedrock includes but is not limited to limestone, dolomite, sandstone, shale and igneous and metamorphic rock.

(6) "Bentonite" means a clay consisting of at least 85% sodium montmorillonite. Bentonite is available in the following forms:

(a) "Bentonite powder" means 200 mesh pure bentonite, without additives.

(b) "Bentonite granules" means 8 mesh pure bentonite, without additives.

(c) "Bentonite pellets" means commercially manufactured tablets made by compressing pure bentonite, without additives, into forms greater than $\frac{1}{4}''$ in size.

(d) "Bentonite chips" means commercially processed angular fragments of pure bentonite, without additives.

(7) "Bentonite — cement grout" means a mixture with the ratio of 5 pounds of bentonite with 94 pounds of Portland cement and 8.5 gallons of water from a known safe and uncontaminated source.

(8) "Bentonite — fine sand slurry" means a mixture with the minimum ratio of 50 pounds of bentonite with 100 gallons of water from a known safe and uncontaminated source and 10−25% sand by volume for a mud weight of 11 pounds per gallon.

(9) "Borehole" means a circular hole deeper than it is wide, constructed in earth material for the purpose of either installing a well or obtaining geologic or groundwater related data. Boreholes are also referred to as drillholes.

(10) "Clay" means an inorganic soil with low permeability characteristics and a plasticity index of 7 or more.

(11) "Coarse sand" means a well sorted sand with a predominant grain size between 4.76mm and 2.0mm as established by the unified soil classification system.

(12) "Concrete" means a slurry mixture with a ratio of 94 pounds of cement, equal volumes of dry sand and gravel and 5 to 6 gallons of water from a known safe and uncontaminated source. The ratio of sand and gravel to cement may not exceed 3 parts to one.

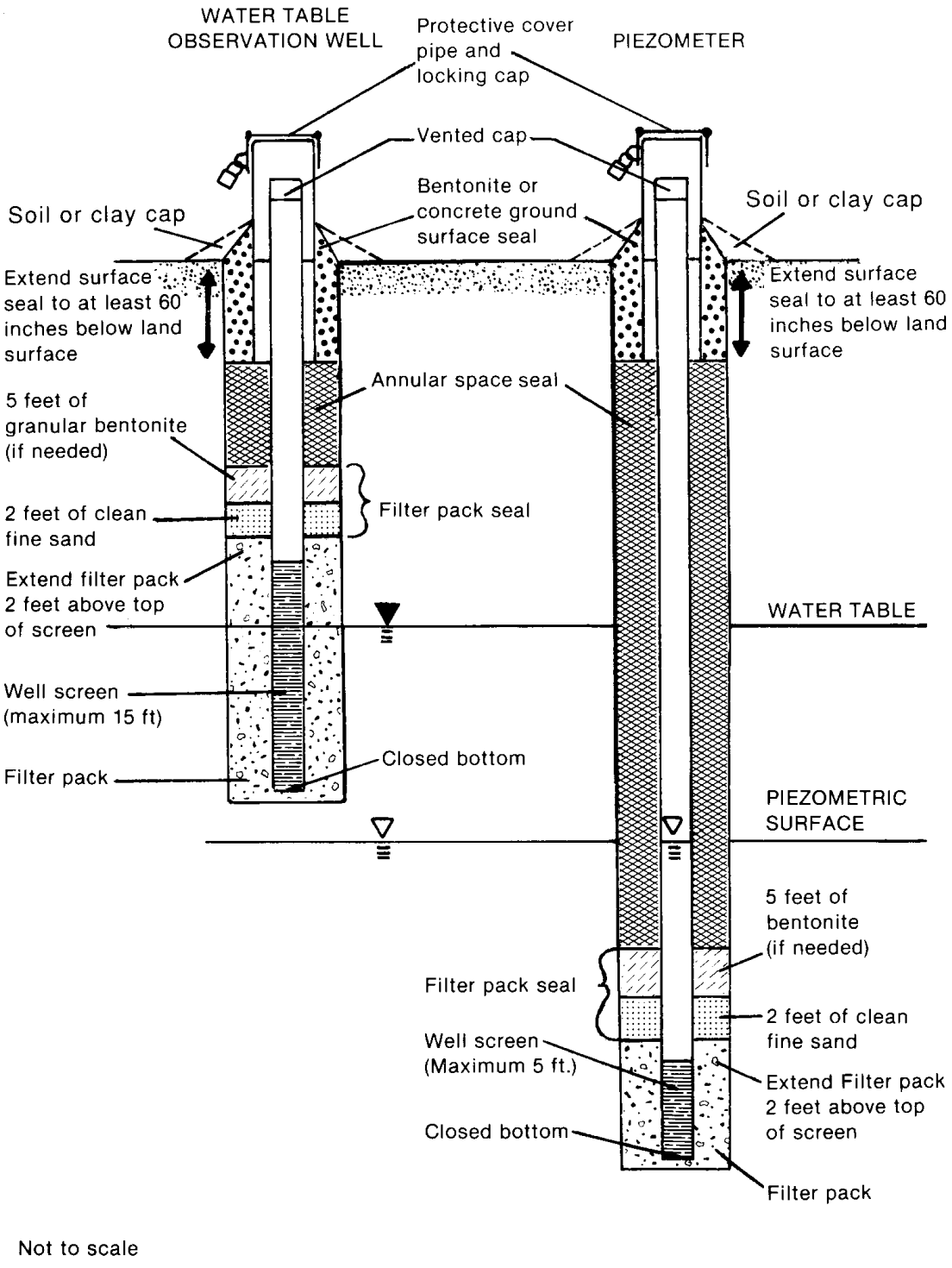
(13) "Department" means the department of natural resources.

(14) "Driven point well" means a well constructed by joining a drive point with lengths of pipe and driving the assembly into the ground with percussion equipment or by hand, without first removing material below the 10 foot depth.

(15) "Filter pack" means the sand, gravel or both placed in direct contact with the well screen.

(16) "Filter pack seal" means the sealing material placed in the annular space above the filter pack and below the annular

Figure 1.
Typical water table observation well and piezometer construction details.



History: Cr. Register, January, 1990, No. 409, eff. 2−1−90; am. (1), Register, June, 1991, No. 426, eff. 7−1−91.

APPENDIX C

EXAMPLE BLANK COCs

Pace Analytical®
www.pacelabs.com

AIR: CHAIN-OF-CUSTODY / Analytical Request Document

The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately.

Page: of

Section A
Required Client Information:

Company:	
Address:	
Email To:	
Phone:	Fax:
Requested Due Date/TAT:	

Section B
Required Project Information:

Report To:
Copy To:
Purchase Order No.:
Project Name:
Project Number:

Section C
Invoice Information:

Attention:
Company Name:
Address:
Pace Quote Reference:
Pace Project Manager/Sales Rep.
Pace Profile #:

Program

UST Superfund Emissions Clean Air Act
Voluntary Clean Up Dry Clean RCRA Other_____

Location of Sampling by State _____

Reporting Units
ug/m³___ mg/m³___
PPBV___ PPMV___
Other___

Report Level II.___ III.___ IV.___ Other_____

'Section D Required Client Information

AIR SAMPLE ID
Sample IDs MUST BE UNIQUE

Valid Media Codes

MEDIA	CODE
Tedlar Bag	TB
1 Liter Summa Can	1LC
6 Liter Summa Can	6LC
Low Volume Puff	LVP
High Volume Puff	HVP
Other	PM10

ITEM #	'Section D Required Client Information / AIR SAMPLE ID	MEDIA CODE	PID Reading (Client only)	COLLECTED: COMPOSITE START END/GRAB DATE	COLLECTED: COMPOSITE START END/GRAB TIME	COLLECTED: COMPOSITE - DATE	COLLECTED: COMPOSITE - TIME	Canister Pressure (Initial Field - psig)	Canister Pressure (Final Field - psig)	Summa Can Number	Flow Control Number	Method: PM10	3C- Fixed Gas (%)	TO-3	TO-3M (Methane)	TO-4 (PCBs)	TO-13 (PAH)	TO-14	TO-15	TO15 Short List*	Pace Lab ID
1																					
2																					
3																					
4																					
5																					
6																					
7																					
8																					
9																					
10																					
11																					
12																					

Comments :

RELINQUISHED BY / AFFILIATION	DATE	TIME	ACCEPTED BY / AFFILIATION	DATE	TIME

SAMPLE CONDITIONS

	Y/N	Y/N	Y/N
	Y/N	Y/N	Y/N
	Y/N	Y/N	Y/N
	Y/N	Y/N	Y/N
Temp in °C	Received on Ice	Custody Sealed Cooler	Samples Intact

SAMPLER NAME AND SIGNATURE

PRINT Name of SAMPLER:

SIGNATURE of SAMPLER: DATE Signed (MM / DD / YY)

UPPER MIDWEST REGION
MN: 612-607-1700 **WI:** 920-469-2436

Pace Analytical®
www.pacelabs.com

CHAIN OF CUSTODY

COC No.

(Please Print Clearly)	
Company Name:	
Branch/Location:	
Project Contact:	
Phone:	
Project Number:	
Project Name:	
Project State:	
Sampled By (Print):	
Sampled By (Sign):	
PO #:	**Regulatory Program:**

Quote #:	
Mail To Contact:	
Mail To Company:	
Mail To Address:	
Invoice To Contact:	
Invoice To Company:	
Invoice To Address:	
Invoice To Phone:	

***Preservation Codes**
A=None B=HCL C=H2SO4 D=HNO3 E=DI Water F=Methanol G=NaOH
H=Sodium Bisulfate Solution I=Sodium Thiosulfate J=Other

Data Package Options (billable)
- ☐ EPA Level III
- ☐ EPA Level IV

MS/MSD
- ☐ On your sample (billable)
- ☐ NOT needed on your sample

Matrix Codes

A = Air	W = Water
B = Biota	DW = Drinking Water
C = Charcoal	GW = Ground Water
O = Oil	SW = Surface Water
S = Soil	WW = Waste Water
Sl = Sludge	WP = Wipe

PACE LAB #	CLIENT FIELD ID	COLLECTION DATE	COLLECTION TIME	MATRIX	FILTERED? (YES/NO) PRESERVATION (CODE)* Y / N	Pick Letter	Analyses Requested	CLIENT COMMENTS	LAB COMMENTS (Lab Use Only)	Profile #

Rush Turnaround Time Requested - Prelims
(Rush TAT subject to approval/surcharge)
Date Needed:

Transmit Prelim Rush Results by (complete what you want):

Email #1:	
Email #2:	
Telephone:	
Fax:	

Samples on HOLD are subject to special pricing and release of liability

Relinquished By:	Date/Time:	Received By:	Date/Time:
Relinquished By:	Date/Time:	Received By:	Date/Time:
Relinquished By:	Date/Time:	Received By:	Date/Time:
Relinquished By:	Date/Time:	Received By:	Date/Time:
Relinquished By:	Date/Time:	Received By:	Date/Time:

PACE Project No.

Receipt Temp = °C

Sample Receipt pH
OK / Adjusted

Cooler Custody Seal
Present / Not Present
Intact / Not Intact

Version 6.0 06/14/06