Site-Specific Quality Assurance Project Plan: Phase II Environmental Site Assessment Long Falls Paperboard

RFA #17023

161 Wellington Road
Brattleboro, Vermont
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PROJECT NO.

19-0015

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1. Form A: Title and Approval Page

Site-Specific Quality Assurance Project Plan: Phase II Environmental Site Assessment, Long Falls Paperboard, Brattleboro, Vermont

Document title

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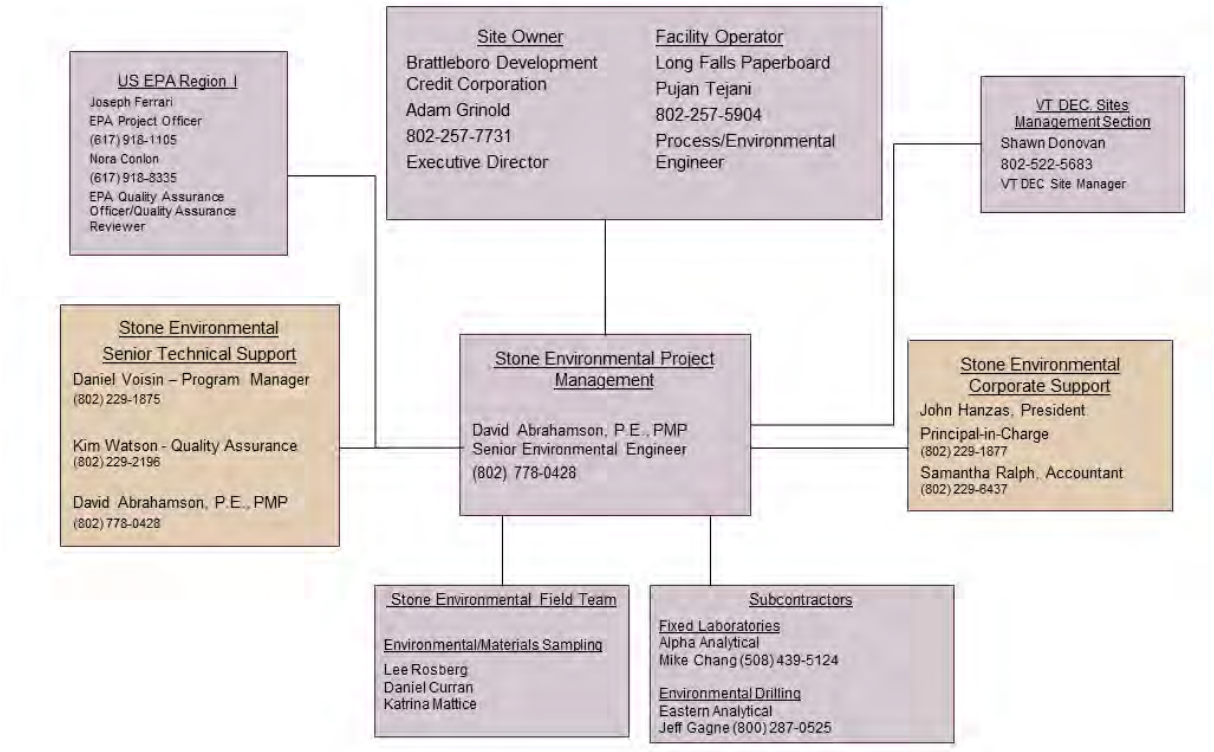
2. Form B: Project Organization and Responsibilities

Figure 1: Project Organizational Chart



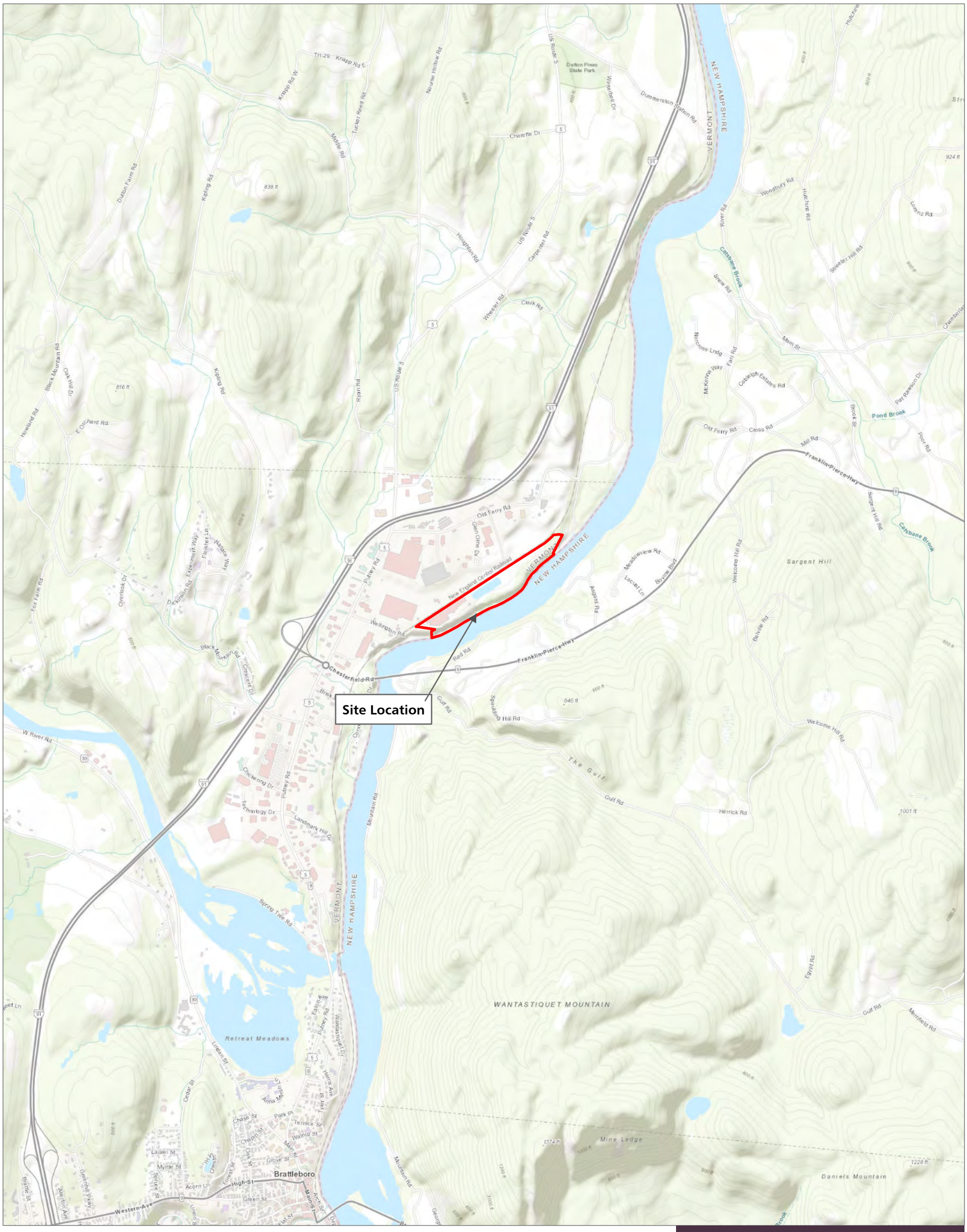
3. Form C: Problem Definition

This Site-Specific Quality Assurance Project Plan (SSQAPP) along with the Brownfields Assessment (BA) Generic QAPP on file with the Vermont Department of Environmental Conservation (VT DEC) and United States Environmental Protection Agency (EPA) Region I (RFA#17023) constitute the work plan and field and analytical quality assurance plan for a Phase II Environmental Site Assessment (ESA) at the Long Falls Paperboard (LFP) property located at 161 Wellington Road in Brattleboro, Vermont (the Site, Figure 2). This SSQAPP was prepared by Stone Environmental (Stone) on behalf of VT DEC and Town of Brattleboro, Vermont. This SSQAPP has been prepared in accordance with the VT DEC Investigation and Remediation of Contaminated Properties Rule (IRule) and serves as the work plan for VT DEC review.

On or about December 31, 2018, Brattleboro Development Credit Corporation (BDCC) purchased the Site from Neenah, the entity that operated the paperboard facility at the Site since purchasing it from FiberMark in 2015. Concurrent with BDCC's purchase of the Site, Long Falls Paperboard (LFP) became the Site occupant and took over facility operations. LFP plans to purchase the Site from BDCC in 2019 upon completion of environmental due diligence. Environmental consultants performed several Phase I ESAs and Limited Environmental Compliance Reviews on behalf of FiberMark, the most recent in 2015. In support of BDCCs' purchase of the property, LE Environmental, LLC (LEE) was retained to perform a Phase I ESA (2018 LEE) as part of environmental due diligence prior to purchase. BDCC applied for an exemption from liability under Vermont's Brownfields Reuse and Environmental Liability Limitation Act (BRELLA) and as such, has been provided certain liability protections under BRELLA as an 'innocent current owner' and through the Regional Development Corporation exemption.

Performed in late 2018, LEE's Phase I ESA identified 12 Recognized Environmental Conditions (RECs) in connection with the Subject Property (2018 LEE):

1. Documented No. 6 fuel oil release (historical REC and REC) due to leaking underground storage tanks (USTs).
2. Potential petroleum contamination due to diesel and gasoline USTs removed in 1988.
3. Use of the property for paper manufacturing for 58 years, which may have resulted in soil, groundwater and/or soil vapor contamination. Potential contaminants of concern include volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), metals, dioxin, and perfluorinated chemicals (PFCs).
4. Potential chemical and petroleum discharge to basement floor sumps and underground piping of unknown integrity possibly resulting in releases via piping breaches.
5. Visible and potential releases from equipment in the storage yard.
6. Potential for subsurface contamination due to an abandoned drum.
7. Filled area at the north end of the property with undocumented fill materials.
8. Windham Solid Waste Management District (WSWMD) landfill documented and potential influence on the property's groundwater quality (Controlled REC).
9. Potential soil and groundwater contamination from the active septic system north of the mill.
10. Potential soil and groundwater contamination from the unused septic system east of the mill.



LEGEND

Target Property Boundary

N

0 1,000 2,000

Feet

Figure 2 Site Location

Long Falls Paper Phase II
Environmental Site Assessment

Prepared for
Vermont Department of Environmental Conservation

STONE ENVIRONMENTAL

Source: Esri World Imagery

Path: O:\PROJ-19\EAR\19-015 Long Falls Paper Phase II ESA\GIS\MapDocuments\PresentationsAndReports\19-015 Long Falls Paper Phase II ESA\19-015 Long Falls Paper Phase II ESA.aprx Site Location 11x17
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11. Potential contamination in connection with the active rail line adjoining the west side of the facility.
12. Potential releases of hazardous substances and/or petroleum products from the historical printing press adjoining the property to the west.

A detailed summary of previous environmental investigations is provided in Section 3.3.

The Phase II ESA is designed to evaluate whether the RECs listed above constitute an actual release of petroleum or hazardous materials to the environment. Additionally, while the wastewater treatment lagoons were not deemed to be a REC (2018 LEE), VT DEC has requested that it be added as a REC and be addressed by the Phase II ESA.

3.1. Site Description

According to the historical records reviewed (Section 3.3) the Site is located at 42°53'22.34" north latitude 72°32'234.28" west longitude and is situated on a 39.52-acre parcel of land located at 161 Wellington Road in Brattleboro, Vermont (Figure 2). A Site Vicinity Map is provided as Figure 3. Site Maps with investigation locations are provided as Figures 4 and 5. The Site includes an approximately 200,000-square foot paper manufacturing plant, an associated wastewater treatment plant, and a sand filter house (Figure 3). The manufacturing facility is a concrete and metal structure with a partial basement and partial second floor. The facility was constructed in 1960, with several additions being constructed between the late 1960s and late 1990s. The wastewater treatment plant is composed of a clarifier that discharges to four aerated treatment lagoons. Liquid effluent from the lagoons is discharged to the Connecticut River. The sand filter house is a single-story structure constructed of cement blocks and contains a disinfection unit. This building was constructed in 1996 to treat process water from the Connecticut River.

The Site is generally flat and is situated on an alluvial terrace of the Connecticut River, and is zoned for industrial use. Process water for the plant is pumped primarily from the Connecticut River; the plant is also served by two on-site backup process water supply wells. The facility is connected to the municipal water system. The bathrooms and laboratory are served by an on-site septic system.

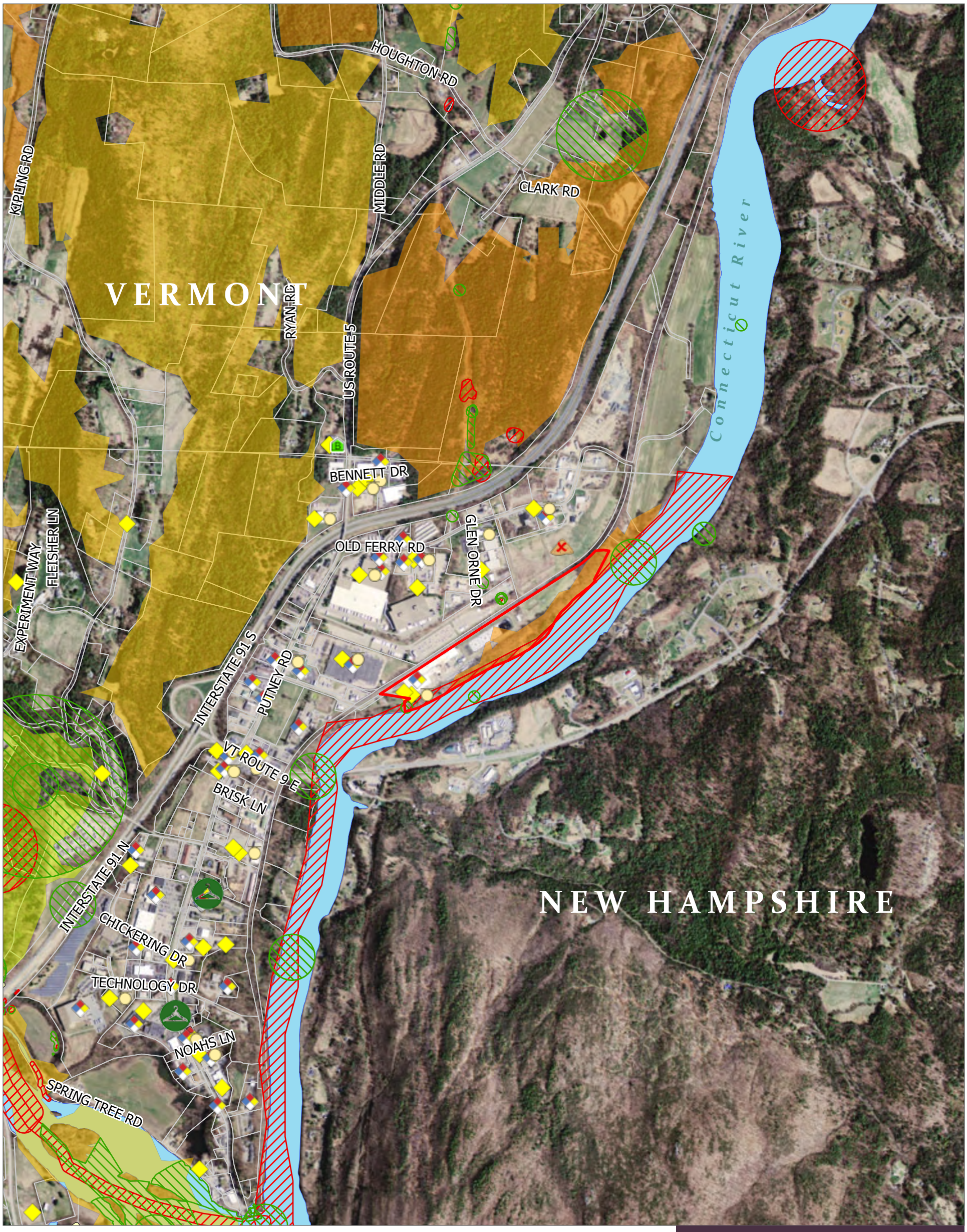
The Site is bound to the east by the Connecticut River, to the north by an undeveloped woodland, to the south by an electrical substation and Wellington Road, and to the west by several commercial properties, including: the BDCC Business Park, Suburban Propane, C&S Wholesale Grocers, and the former Windham Solid Waste Management District Landfill.

3.2. Site History

According to Ramboll (2015 Ramboll), the Site has been in continuous use as a paper mill since it was originally developed in 1960 by Case Brothers which operated at the Site until 1967 at which time it was acquired by Boise Cascade. The facility was operated by Boise Cascade until 1989 when the name was changed to Specialty Paper Board, Inc, which ultimately was renamed as FiberMark, Inc. in 1998. FiberMark filed for bankruptcy in 2004 and reemerged under new ownership of Silver Point Capital in 2006 before subsequently being acquired by America Securities in 2008. The FiberMark business was sold to Neenah in 2015 and operated as Neenah until purchase by BDCC in December 2018.

3.3. Prior Environmental Investigations

The following subsections provide brief summaries of previous environmental-related studies for the Long Falls Paperboard facility.



LEGEND

- Target Property Boundary
- Parcels
- Waterbody
- Underground Storage Tank (working)
- Brownfields
- Dry Cleaner
- Hazardous Waste Generators
- Hazardous Waste Site
- Landfill - CLOSED

Rare, Threatened, Endangered Species and Significant Natural Communities

- Threatened or Endangered
- Rare
- Significant Natural Communities

Habitat Blocks and Wildlife Corridors

- 6 - Higher Priority
- 4
- 3 - Lower Priority

N

0 650 1,300

Feet

Source: Esri World Imagery, VCGI, VTANR

Path: O:\PROJ-19\EAR\19-015 Long Falls Paper Phase II ESA\GIS\MapDocuments\PresentationsAndReports\19-015 Long Falls Paper Phase II ESA\19-015 Long Falls Paper Phase II ESA.aprx Vicinity Map Exported: 5/20/2019 1:32 PM by wrich

Figure 3 Vicinity Map

Long Falls Paper Phase II
Environmental Site Assessment

Prepared for
Vermont Department of Environmental Conservation

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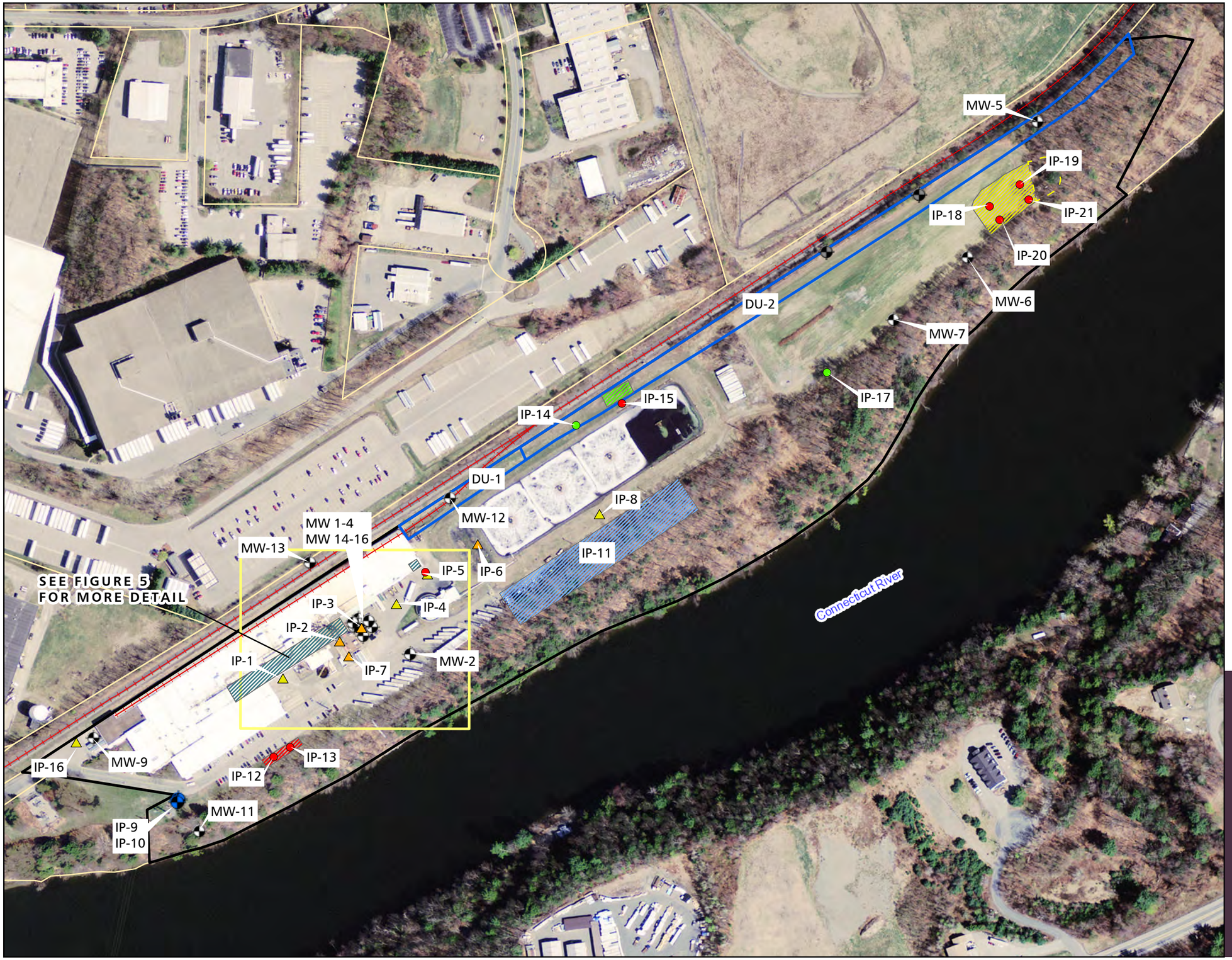

N

0 150 300

Feet

LEGEND

- Target Property Boundary
- Inset Extent
- Rail Line
- All Parcels
- ISM Decision Unit
- Basement Area
- Active Fill Area
- Outdoor Equipment Area

Leaching Bed

- Active
- Former

Proposed Sample Location

- Groundwater
- Subsurface Soil
- Subsurface Soil & Groundwater
- Surface Soil

Existing Well

- Monitoring Well
- Production Well
- Windham SWMD Well

Locations of all map elements are approximate

Source: Esri World Imagery, Stone Environmental, VCGI

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Figure 4 Proposed Investigation Locations

Long Falls Paper
Phase II Environmental Assessment

Prepared For
Vermont Department of Environmental Conservation

STONE ENVIRONMENTAL

N

0 25 50

Feet

Target Property Boundary

LEGEND

- TargetPropertyBoundary
- Rail Line
- BasementArea
- Monitoring Well (Existing)

Proposed Sample Location

- Groundwater
- Subsurface Soil
- Subsurface Soil & Groundwater
- Surface Soil

Locations of all map elements are approximate

Source: Esri World Imagery, Stone Environmental

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Figure 5 Proposed Investigation Locations (Inset)

Long Falls Paper
Phase II Environmental Assessment

Prepared For
Vermont Department of Environmental Conservation

STONE ENVIRONMENTAL

3.3.1. 1989 – 2015 Various Environmental Assessments, Phase I ESAs and Environmental Compliance Reviews

Several environmental assessments, including Phase I ESAs and Limited Environmental Compliance Reviews, were performed on behalf of the owner and/or operator of the facility, the earliest available of which was performed in 1989 and the most recent in 2015. These assessments have been generally referenced in each subsequent assessment, including LEE's 2018 Phase I ESA, so the results of those assessments are not individually summarized. The available assessments include:

- Boise Cascade Corporation, Environmental Compliance Audit, Pressboard Products Mill, Brattleboro, Vermont, performed by C-E Engineering, May 1989
- Phase I ESA, Limited ACM and SVM Survey and Regulatory Compliance Review, FiberMark, performed by Tighe & Bond, November 2007
- Phase I Environmental Site Assessment and Limited Environmental Compliance Review of FiberMark, Inc., prepared by ENVIRON International Corporation, December 2007
- Phase I Environmental Site Assessment, FiberMark, prepared by Clayton Group Services, Inc., September 2003
- Phase I Environmental Site Assessment and Limited Environmental Compliance Review, FiberMark North America Inc., prepared by Ramboll Environ US Corporation, June 2015

3.3.2. 1990 – 1994 No. 6 Fuel Oil Release Investigation Reports

In February 1990, two 25,000 gallon No. 6 fuel oil USTs were excavated and removed from the property. Griffin International, Inc. (Griffin) performed a site investigation in 1990 and follow-up monitoring in 1994, recommending that the Site be considered for a Site Management Activities Complete (SMAC) designation, which was reportedly granted in 1994. Available documentation includes:

- Report on the Investigation of Subsurface Petroleum Contamination, Specialty Paperboard, Brattleboro, Vermont performed by Griffin International, Inc., July 1990
- Report on August 1994 Groundwater Sampling and Analysis for Specialty Paperboard, Brattleboro, Vermont performed by Griffin International, Inc., October 1994.

3.3.3. LE Environmental Phase I ESA, December 2018

LEE completed a Phase I ESA on December 12, 2018 of the Neenah Paper Manufacturing facility on behalf of the BDCC (2018 LEE). The Phase I was performed using the *Standard Practice for Environmental Site Assessments: Phase I ESA Assessment Process*, published by ASTM International as Standard Practice E1527-13. The Phase I was performed as part of environmental due diligence in anticipation of purchasing the property. The Phase I ESA revealed no evidence of RECs in connection with the property, except for the following:

1. Documented No. 6 fuel oil release (historical REC and REC) due to leaking USTs.
2. Potential petroleum contamination due to diesel and gasoline USTs removed in 1988.
3. Use of the property for paper manufacturing for 58 years, which may have resulted in soil, groundwater and/or soil vapor contamination. Potential contaminants of concern include volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), metals, dioxin, and perfluorinated chemicals (PFCs).
4. Potential chemical and petroleum discharge to basement floor sumps and underground piping of unknown integrity possibly resulting in releases via piping breaches.
5. Visible and potential releases from equipment in the storage yard.
6. Potential for subsurface contamination due to an abandoned drum.

7. Filled area at the north end of the property with undocumented fill materials.
8. Windham Solid Waste Management District (WSWMD) landfill documented and potential influence on the property's groundwater quality (Controlled REC).
9. Potential soil and groundwater contamination from the active septic system north of the mill.
10. Potential soil and groundwater contamination from the unused septic system east of the mill.
11. Potential contamination in connection with the active rail line adjoining the west side of the facility.
12. Potential releases of hazardous substances and/or petroleum products from the historical printing press adjoining the property to the west.

LEE made the following recommendations further assessment to determine whether these RECs constitute an actual release to the environment:

1. The Phase II ESA should include soil, groundwater and soil gas testing. Chlorinated VOC (CVOC) detections in groundwater at 70-foot depth suggest there is a source of CVOCs in the nearby soils.
2. Groundwater monitoring wells from the previous site investigation may be present beneath the pavement. These wells were 70-80 feet deep and in light of the cost of replacement, a geophysical survey to attempt to locate the buried wells might be cost effective.
3. Groundwater beneath the northern portion of the property in the Class IV zone is non-potable and its investigation may be less of a priority than elsewhere on the property. The contents of the fill area should be evaluated via backhoe test pits to determine if hazardous substances and/or petroleum products are present and whether there is soil contamination.
4. A video evaluation of the basement sump and piping system could provide useful information on the condition of the piping and whether there are breaches that should be evaluated for soil contamination.

3.3.4. Weston & Sampson Limited PFAS Sampling – December 2018

On December 12, 2018, Weston & Sampson (W&S) collected a sample of wastewater treatment plant biosolids and submitted it for per- and polyfluoroalkyl substances (PFAS) analysis as well as synthetic precipitation leaching procedure (SPLP) for PFAS (2018 WSE). W&S also collected groundwater samples from the two on-Site facility production wells and liquid samples of the wastewater treatment plant effluent and lagoon liquids and submitted them to a laboratory for PFAS analysis. PFASs were not detected in the biosolids sample, however, Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA) and perfluorooctanesulfonic acid (PFOS) were detected in the biosolids SPLP analysis sample above the method detection limit, but below the method reporting limit, at estimated concentrations of 6.19 nanograms per liter (ng/L), 4.00 ng/L and 4.11 ng/L, respectively. Perfluorooctanoic acid (PFOA) and PFOS were detected in the wastewater treatment plant effluent sample at concentrations of 2.59 (estimated) and 17.1 ng/L, respectively. PFBA, perfluorohexanoic acid (PFHxA) and PFOS were detected in the liquid sample collected from the lagoon at concentrations of 4.13 ng/L (estimated), 8.02 ng/L and 10.2 ng/L (estimated), respectively.

3.4. Conceptual Site Model

The following Conceptual Site Model (CSM) provides a set of working hypotheses that describe key aspects of the Site. As with any hypothesis, the CSM will require additional testing to arrive at the desired level of confidence. The CSM includes a discussion of the known physical, geologic, and hydraulic attributes of the Site and surrounding area, how chemicals were released at the Site, their transport pathways, fate mechanisms, and potential routes of exposure to ecological and human receptors. The CSM provides the context from which the site investigation is developed and a framework to make sound Site management decisions.

3.4.1. Geology and Hydrogeology

According to the Agency of Natural Resource (ANR) Atlas, the Site is underlain by schist (primary) and metawacke (secondary). The bedrock is described as dark gray to coaly-black, fine-grained plagioclase-muscovite-quartz schist and metawacke, shown southeast of Springfield, in part correlative with staurolite-grade rocks mapped as Littleton Formation. Bedrock was reported at depths of 137 and 142 feet below ground surface in two bedrock wells drilled to the west and southwest of the Site where ground surface elevations are relatively similar to that of the Site. Overburden groundwater production wells at the Site were drilled to approximately 100 feet below ground surface (ft bgs). Therefore, it is anticipated that bedrock would be encountered between 100 and 150 fbgs at the Site. Depth to water is approximately 70 ft bgs at the Site.

Overburden soils at the Site are mapped as fluvial sands. In an appendix to the 2015 Ramboll Environ Phase I ESA, Griffin International, Inc. (Griffin) reported in their "Report on the Investigation of Subsurface Petroleum Contamination, Specialty Paperboard, Brattleboro, Vermont" dated July 1990 (1990 Griffin), that subsurface soils consisted of "nearly horizontal stratigraphic sequences, each measuring approximately one-foot thick and that they begin as coarse, well rounded, well sorted sand at the top and grade into fine, silty sand at the bottom" of each sequence. Griffin further concluded that the stratigraphic sequence planes dip slightly to the south. We interpret these sequences to be representative to fore-set beds lain as a delta within Glacial Lake Hitchcock which occupied the Connecticut River Valley between Middletown, Connecticut and Burke, Vermont between 15,000 and 12,000 years before present. As fore-set beds, the observed stratigraphic sequences are likely underlain by finer couplets typical of bottom-set beds and possibly varve deposits. Following the draining of Lake Hitchcock, the post-glacial Connecticut River down cut through the deltaic sediments and reworked the deposits to remove finer materials, resulting in the fluvial sands at the surface, as mapped.

Ground surface at the Site is generally flat, except along the Connecticut where the land slopes steeply downward approximately 70 feet toward the Connecticut. Ground surface in the surrounding area north and northwest of the Site generally slopes to the south and east. Based on surrounding area topography, groundwater flow would be presumed to be east or southeast toward the Connecticut. In Griffin's 1990 report, Griffin noted previous subsurface investigations conducted for Windham Regional Landfill located to the northwest of the Site indicated the Connecticut is a losing stream in the vicinity of the paper mill; however, a groundwater contour map provided by Griffin in 1994 indicated groundwater surface gradient toward the river. While over eight miles downstream, a dam impounds water that appears to reach well upriver of LFP property, towards the dam located upriver in Bellows Falls. Based on this information, and in the absence of multiple rounds of groundwater and surface water level data, we would expect the Connecticut to be both a losing and gaining stream near the LFP property, depending on groundwater levels and recharge.

3.4.2. Contaminant Sources and Release Mechanisms

Based on Stone's review of existing information, the only known documented contaminant releases at the Site are from various petroleum surface spills and releases from leaking No. 6 fuel oil USTs. Reported petroleum spills were generally contained (with the exception of a reported release that impacted the on-site clarifier) and the no. 6 fuel oil leaking UST release received a VT DEC Site Management Activities Complete letter in 1994. However, soil and groundwater were not sampled for the primary constituents of no. 6 fuel oil, polynuclear aromatic hydrocarbons (PAHs). Additionally, detections of CVOCs in groundwater samples collected during the No. 6 fuel oil investigation from 1990 to 1994 indicate undocumented releases of CVOCs at the Site and/or at an unknown upgradient source; this could be an indication of a release mechanism for other contaminants of concern at the Site that have not been investigated.

Other potential COCs include volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), metals, dioxins, and per-fluorinated chemicals (PFCs) (LEE Phase I). Stone notes that PFCs contain a wide range of compounds, some non-toxic, and this term should be updated to the more recently studied and regulated PFAS. In regard to metals, it is known that copper is used at the facility and titanium was used historically, along with aluminum and sodium compounds.

3.4.3. Contaminant Distribution, Fate, and Transport

Contaminants and potential contaminants of concern, source and release mechanisms, and media of interest, organized by REC, are outlined in Table 1. General information on fate and transport for the Site COCs follows.

VOCs and SVOCs may have been used in facility processes and are found in hydraulic fluids, fuel oil, gasoline, diesel fuels and in chemicals historically used at the facility. VOCs and SVOCs include compounds that have been identified as carcinogenic and/or mutagenic. Some VOCs readily dissolve in groundwater and therefore migrate with groundwater. VOCs in fuels tend to be lighter than water and will float in non-aqueous forms. CVOCs are heavier than water and will sink in non-aqueous forms. SVOCs are not as volatile as VOCs and tend to sorb to soil particles more than VOCs.

Per- and polyfluoroalkyl substances (PFAS) have been used historically in paper coatings – among other uses – and, as previously noted, were recently detected in the facility wastewater treatment liquid effluent and the SPLP analysis on the biosolids sample. Some PFASs can adsorb to material with high organic content, but in general, they are very soluble and tend to move with groundwater.

Dioxins and furans are produced during pulp bleaching operations. Dioxins and furans are highly toxic and are known human carcinogens. Dioxins and furans are extremely persistent in the environment and tend to stay strongly sorbed to soil, especially those with a high organic content. The LFP facility currently does not bleach pulp, although a chemical bleaching process was used in color stripping in the 1960s and was discontinued in the 1970s (2015 Ramboll). Dioxins are known to be present in paper pulp that has been bleached. If pulp that was bleached was used at the plant, then dioxins may have been present, most likely in the facility waste sludge, and wherever these sludges were disposed.

PCBs may have been present in machinery hydraulic fluids and oils, as well as potentially on recycled paper imported to the facility that contain dyes or carbonless paper. PCB oil and fluids containing PCBs could have migrated to the building sumps and potentially the subsurface. Like dioxins, PCBs are extremely persistent in the environment.

Table 1: Conceptual Site Model

LE Environmental Phase I ESA RECs	Source and Potential Sources, Release and Transport Mechanisms	COCs	Media of Interest
REC 1: No. 6 Fuel Oil Release	No. 6 fuel oil leaked from USTs to soil and to groundwater. Primarily adsorbed phase in soils w/ LNAPL 1990 - 1994. This documented release received a Site Management Activities Complete (SMAC) in 1994. There is no known soil analytical data for this release. Groundwater was previously sampled for purgeable halocarbons and aromatics (Methods 601 & 602); groundwater was not sampled for SVOCs, specifically PAHs.	VOCs, SVOCs	Subsurface soil Groundwater Soil gas
REC 2: Diesel and Gas USTs Removed in 1988	3 USTs (2 gasoline and 1 diesel) were removed in 1988 and were approximately 14 years old at that time. Condition of 1 gasoline UST was good; the other 2 were noted as 'rusted', however, the tank pull form did not note any observed leaks. MTBE had been detected in on-site groundwater in the area of the No. 6 fuel oil tanks and in a groundwater monitoring well MW-11, near the facility production wells; this may indicate on or off-site, upgradient release(s) of gasoline to groundwater. If released on-site, petroleum is potentially adsorbed to soils and in dissolved phase in groundwater. There is also a potential for LNAPL.	VOCs, SVOCs.	Subsurface soil Groundwater Soil gas
REC 3: Use of Property for Paper Manufacturing for 58 Years - may have resulted in soil, groundwater and/or soil vapor contamination	Process and facility liquids are discharged to floor drains & sumps, through conveyance piping, to clarifier. Contaminants to sludge and/or waste treatment system discharge. Possible leaks in floor drains and sumps & conveyance piping to subsurface soils and potentially groundwater. Possible site disposal of sludge. See REC 7 below (former 'Active Fill Area').	VOCs, SVOCs, dioxins/furans, PCBs, PFAS, metals.	Surface soil Subsurface soil Groundwater Soil gas
REC 4: Releases to Basement Floor Sumps and Underground Piping of Unknown Integrity	Process and facility liquids to floor drains & sumps, through conveyance piping, to clarifier. Additionally, the discharge location of the floor drain located in the maintenance area is unknown. VOCs, SVOCs, PFAS and metals would likely migrate to and through groundwater. PCBs and dioxins would tend to stay in the solids and/or adsorbed to soils near the release point. Runoff from sludge storage in the area outside of the clarifier building is collected and is returned to the clarifier; however, the stormwater manhole may not be water tight and cracks in the pavement were observed here, creating a potential pathway to subsurface soils and groundwater.	VOCs, SVOCs, dioxins/furans, PCBs, PFAS, metals.	Subsurface soil Groundwater Soil gas
REC 5: Equipment Storage Yard	Petroleum, oil, and/or hydraulic fluid leaks from equipment release to surface soils and potential release to subsurface soils. Hydraulic fluids historically could have contained PCBs. Due to depth to groundwater, groundwater impacts are not anticipated from limited surface spills, but would be a concern if a substantial release had occurred.	VOCs, SVOCs, PCBs.	Surface soil Subsurface soil Groundwater
REC 6: Abandoned Drum	Drum labeled 'Sartomer" - specialty acrylates and methacrylates monomers and oligomers. Sartomer currently produces acrylates. If the drum contained raw product or other materials when disposed, materials could have discharged to surface soils and potentially subsurface soils, and groundwater.	VOCs	Surface soil Subsurface soil Groundwater
REC 7: Fill at North End of the Property	Observed materials on surface consistent with construction debris in the LEE 2018 Phase I ESA, however, it was labeled an active fill area in a 1989 property survey. If material other than clean construction debris was deposited (e.g. wastewater treatment plant sludge), contaminants could migrate to soil and possibly groundwater.	N/A if only construction debris. If unidentified material is discovered, COCs may include VOCs, SVOCs, dioxins/furans, PCBs, PFAS, metals.	Fill Surface soil Subsurface soil Groundwater
REC 8: WSWMD Landfill Documented Influence on the Property's Groundwater Quality -	Contaminants in leachate from WSWMD landfill has migrated in groundwater beneath the northern portion of the Site. As, Fe, Mn, VOCs determined to exist above state groundwater protection standards at the Site. PFASs detected in groundwater upgradient of the Site, but below current advisory levels.	VOCs, SVOCs, dioxins/furans, PCBs, PFAS, metals.	Groundwater

LE Environmental Phase I ESA RECs	Source and Potential Sources, Release and Transport Mechanisms	COCs	Media of Interest
identified as a controlled REC			
REC 9: Active Septic System - North of the Mill (Installed in 1973) - including stressed vegetation area in vicinity of leach field.	Sanitary and laboratory wastes to septic system. Leachate to subsurface soils and groundwater. Possible surfacing of leachate in area of stressed vegetation.	VOCs, SVOCs, PCBs, PFASs, metals.	Surface soils (stressed vegetation areas) Subsurface soils Groundwater
REC 10: Unused Septic System Area East of the Mill	Sanitary and laboratory wastes to septic system. Leachate to subsurface soils and groundwater.	VOCs, SVOCs, PCBs, PFASs, metals.	Subsurface soils Groundwater
REC 11: Adjacent Railway Line	Deposition of PAHs to surface soils from historic use as railroad. Use of herbicides for vegetation control could potentially impact surface soil.	PAHs, herbicides.	Surface soils
REC 12: Historic Adjoining Printing Press (Book Press)	VOCs and metals, if discharged, could make its way to groundwater and migrate beneath the Site. Note that VOCs were not detected in well MW-9 when sampled for purgeable hydrocarbons in 1994.	VOCs, metals.	Groundwater
REC 13: Wastewater Treatment Plant Lagoons[1]	Any contaminants discharged from the clarifier to the wastewater treatment plant lagoons could potentially leak out of the lagoons if the clay liners had been breached.	VOCs, SVOCs, dioxins/furans, PCBs, PFAS, metals.	Subsurface soil Groundwater Soil gas

[1] REC 13: Wastewater Treatment Plant Lagoons added as a REC by Stone per VT DEC request.

It is known that copper and magnesium is used at the facility and titanium was used historically along with sodium and aluminum compounds. Cyanide may also be a byproduct of the papermaking process. Heavy metals can be present in used machinery oil including lead, cadmium, copper and zinc. Some heavy metals have been identified as carcinogenic and/or mutagenic compounds. Heavy metals typically bind to soil and sediment; however, they can leach into groundwater.

PAHs are a group of chemicals that are common byproducts of the combustion of fossil fuels and occur naturally in fuel oil, coal, and tar and are a subset of SVOCs. Select PAHs have been identified as carcinogenic and/or mutagenic compounds. PAHs do not readily dissolve into water without help from a co-solvent and are therefore slow to migrate to or via groundwater.

Herbicides, including chlorinated herbicides, have been commonly used for agricultural or maintenance purposes including those along the railway right of way and can have carcinogenic and/or mutagenic properties. Herbicides typically bioaccumulate in animal fat and will bind to soil and sediment. They are less soluble in water and do not typically migrate via groundwater.

3.4.4. Sensitive Receptor Evaluation

Known contamination (fuel oil, MTBE and CVOCs) at the Site has been evaluated for its potential for adversely affecting sensitive receptors. Table 2 presents the potentially affected media, pathways, and receptors. This table will be updated based on results of the Phase II ESA and included in the Phase II ESA Report.

Table 2: Sensitive Receptors Evaluation – Known Contaminants

Affected Media	Potential Pathways	Sensitive Receptors/Potential Risk
Surface Water	Overland flow of stormwater runoff and groundwater discharge	Connecticut River / Low – known contaminants are in groundwater.
Surface Soil	Direct contact to contaminated materials	Site users & trespassers / Low – known contaminants are in subsurface soil groundwater.
Sub Surface Soil	Prior fuel spill. Potential for CVOC source area.	Groundwater/Medium Construction workers/Medium
Groundwater	Infiltration of surface water through affected surface soil may leach contaminants.	Potential discharge to Connecticut River/Unknown Potential migration to downgradient locations/Unknown Potential uptake into facility process water/Unknown

Abbreviations: CVOCs- chlorinated volatile organic compounds

3.4.5. Adjoining Property Owners

Adjoining property owners, as presented in the City of Brattleboro 2018 Grand List, are summarized in Table 3, below.

Table 3: Adjoining Property Owner Information

Property Address	Parcel Id	Direction	Owner
153 Wellington Road	00080041.000	Southeast	Green Mountain Power Corp
22 Browne Court	00080035.000	Northeast	Brattleboro Development Credit Corp
89 Glen Orne Drive	00080006.000	North	L & S Associates
109 Glen Orne Drive	00080006.000	North	L & S Associates
111 Glen Orne Drive	00080006.000	North	L & S Associates
54 O'Bryan Drive	00080006.000	North	L & S Associates
47 Old Ferry Road	00080006.000	North	L & S Associates
Old Ferry Road	00080025.000	East	Allard Ruth B Revocable Trust
327-329 Old Ferry Road	00080022.100	Northeast	Windham Solid Waste Management District

4. Form D: Project Description

As stated in Section 3, Form C, the Phase II ESA is designed to assess whether the RECs identified in the January 2019 Phase I ESA have resulted in a release of petroleum or hazardous materials to the environment.

4.1. Site Health and Safety, DigSafe & Existing Well Investigation/ Development

Stone will develop a Site-Specific Health and Safety Plan (HASP) in accordance with 29 CFR 1910.120 and will work under this plan when performing investigative activities at the Site.

Stone will pre-mark each proposed subsurface investigation location for Digsafe utility clearance and obtain a Digsafe ticket for the Site. During this visit, Stone will attempt to obtain facility plans that show underground utilities and features, if they exist. Stone will also attempt to locate monitoring wells identified on previous environmental site investigation reports, including those observed during a Site visit on January 25, 2019. The condition of located wells will be evaluated for usability for hydraulic monitoring and gauged for non-aqueous phase liquid (NAPL) (if present) using an oil-water interface probe. Using known well construction details from prior reports, Stone will determine whether wells can be redeveloped and used to collect quality groundwater samples. Due to the high-density of the underground utilities, including wastewater and natural gas, Stone will also subcontract to an underground utility locator to locate facility-owned features (e.g. water and wastewater treatment plant piping) not marked by Digsafe, as well as attempt to locate any previously unlocated monitoring wells.

Stone proposes to redevelop and complete an elevation survey of monitoring wells, if necessary, during the same mobilization as utility locator oversight. If necessary, monitoring well redevelopment will be completed using a Waterra Hydrolift II pump and all purge water will be contained in 55-gallon drums pending groundwater monitoring results. Stone will again gauge depth to groundwater and LNAPL (if present) in each existing groundwater monitoring well located. Stone will also install a staff gauge in the Connecticut River adjacent to the Site to measure surface water elevation in conjunction with groundwater levels. Data collected will be used to estimate horizontal hydraulic gradients at the Site.

4.2. Soil Assessment

4.2.1. Sub-Surface Soil Borings

To assess the exterior portions of the Site for subsurface soil contamination, Stone will oversee the advancement of up to 12 soil borings in areas of concern using a Geoprobe 7822 DT and closed piston direct push tooling (Geoprobe MC5 or DT325) appropriate for the geological setting and investigation objectives. Soil boring and sample locations will be geographically positioned using a sub-meter global positioning system (GPS).

Soil samples will be collected in accordance with Stone's SOPs and submitted to NELAP accredited Alpha Analytical's (Alpha's) Westboro, Massachusetts laboratory for analysis as indicated in Section 5. Samples

collected for dioxins, PFAS and metals will be transported by Alpha to their NELAP accredited laboratory in Mansfield, Massachusetts for analysis.

4.2.2. Surface Soil

To assess whether the presence of a 55-gallon drum (REC 6) has resulted in a release to the environment, Stone proposes to screen soils near the drum for the presence of VOCs using a photoionization detector (PID).

Hand tooling will be used to collect a surface soil sample from an area of stressed vegetation located to the southwest of the active leach field to evaluate whether Site contaminants of concern have been released in this area.

To assess the outdoor equipment storage area (REC 5), Stone will visually inspect the ground surface for evidence of leaks of oil and/or hydraulic fluid. Stone will use a shovel and hand-driven soil coring tool to assess whether any identified leaks have impacted surface soils beyond the top one or two inches.

Stone proposes to complete surface soil assessments following an incremental sampling methodology (ISM) to evaluate soil quality in two decision units (DUs) for REC 11, DU1 along the Site rail spur and DU2 along the adjacent rail corridor.

Soil boring and sample locations will be geographically positioned using a sub-meter GPS.

Soil samples will be collected in accordance with Stone's SOPs and submitted to NELAP accredited Alpha's Westboro, Massachusetts laboratory for analysis as indicated in Section 5. Samples collected for dioxins, PFAS and metals will be transported by Alpha to their NELAP accredited laboratory in Mansfield, Massachusetts for analysis.

4.3. Groundwater Assessment

To evaluate whether contaminants of concern have entered the subsurface and impacted groundwater, Stone proposes to collect up to 11 groundwater samples using a screen point sampler (Geoprobe SP22 or equivalent) installed using direct push methods described above for soil borings. Five soil boring and groundwater sampling locations will be co-located. Stone also proposes to collect groundwater samples from two on-Site production wells. Groundwater sampling locations will be geographically positioned using a sub-meter GPS. Groundwater samples be collected following low flow sampling techniques in accordance with Stone SOPs and will be submitted to NELAP accredited Alpha's Westboro, Massachusetts laboratory for analysis as indicated in Section 5. Samples collected for dioxins, PFAS and metals will be transported by Alpha to their NELAP accredited laboratory in Mansfield, Massachusetts for analysis.

4.4. Wastewater Treatment Plant Lagoon Sludge Assessment

To evaluate potential contaminants in the sludge generated in the wastewater treatment plant lagoons per VT DEC's request, Stone will collect one sample of the dried sludge from the on-Site stockpile. The sample will be collected and submitted to NELAP accredited Alpha's Westboro, Massachusetts laboratory for analysis as indicated in Section 5. Samples collected for dioxins, PFAS and metals will be transported by Alpha to their NELAP accredited laboratory in Mansfield, Massachusetts for analysis.

4.5. Evaluation of Sampling Results with Action Limits

For this Phase II ESA, the following action limits will be used:

- Soils: VT DEC Soil Screening Values (SSVs) included as Appendix A §35-APX-A1 of the IRule. SSVs include:
  - May 2016 EPA RSLs for residential and industrial soils;
  - Vermont Screening Levels for residential and industrial soil.
- Groundwater: Vermont Groundwater Enforcement Standards (VGES) published as Appendix 1 of Chapter 12 of the Vermont Environmental Protection Rules: Groundwater Protection Rule and Strategy, Emergency Rule, adopted July 2018

Appendix A provides tables with reporting limits for each contaminant of concern and their respective regulatory criteria, specifically:

- Table A.1: VOCs in soil by EPA Method 8260C;
- Table A.2: VOCs in groundwater by EPA Method 8260C; and
- Table A.3: SVOCs and PAHs in soil by EPA Method 8270D, and 8270D-SIM for select analytes;
- Table A.4: SVOCs in groundwater by EPA Method 8270D, and 8270D-SIM for select analytes;
- Table A.5: Dioxins/ Furans in soil by EPA Method 8290A;
- Table A.6: Dioxins/ Furans in groundwater by EPA Method 8290A;
- Table A.7: PCBs in soil by EPA Method 8082A;
- Table A.8: PCBs in groundwater by EPA Method 8082A;
- Table A.9: PFAS in soil by EPA Method 537(M);
- Table A.10: PFAS in groundwater by EPA Method 537(M);
- Table A.11: Metals in soil by EPA Methods 6010D, 7471B, and 4500CN-CE;
- Table A.12: Metals in groundwater by EPA Methods 6010D, 6020B, 7470A, and 9010C/9012B;
- Table A.13: Herbicides in soil by EPA Method 8151A.

4.6. Investigative Derived Waste

Investigation derived wastes (IDW) generated during the Phase II ESA will include purge water, soil cuttings, tubing, decontamination fluids, and soil core liners, as well as personal protective equipment such as gloves. Solid IDW will not require specialized disposal techniques and will be disposed of as municipal waste at the conclusion of fieldwork. All purge water generated during the Phase II ESA will be contained within a US DOT-approved, 55-gallon drum pending analytical results of groundwater samples. If non-petroleum contamination is detected in groundwater, the drum will be disposed in accordance state and federal law. Soil cuttings generated from soil borings will be backfilled to the location where they were generated, and any excess material will be contained within a within a US DOT-approved, 55-gallon drum pending analytical results of soil samples.

4.7. Quality Assurance/Quality Control (QA/QC)

To ensure that data produced during field and analytical efforts are of known and acceptable quality, QA/QC samples will be collected for each medium of interest. Table 4, below, present the anticipated QA/QC samples that will be collected as part of this investigation. Trip blanks will be prepared by the laboratory and accompany each cooler that contains VOC and PFAs samples. Field duplicates will be collected at a 5 percent (1 in 20) frequency. Field quality control requirements are presented on Form M.

Sampling apparatus will be decontaminated prior to initiating sample collection in accordance with Stone Standard Operating Procedure (SOP) SEI 5.1.5. This SOP is included in Appendix D of the BA QAPP.

Table 4: Field Quality Control Requirements

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Field Duplicates	5% per analyte group/ matrix	Precision 50% soil matrices, 30% groundwater matrices	Assess sampling precision, qualify data
Field Blanks	1 per day of groundwater sampling (PFAS only)	Accuracy/ Bias- contamination	Identify source of contamination, qualify data
Equipment Blank	1 groundwater equipment blank (PFAS only)	Accuracy/ Bias- contamination	Identify source of contamination, qualify data
VOA Trip Blank	1 per shipment containing VOC and PFAs samples	Accuracy/ Bias- contamination Target analytes < Quantitation Limit	Identify source of contamination during transit, qualify data

4.8. Reporting

Stone will provide brief daily updates to VT DEC, BDCC and the Town of Brattleboro during field activities. Following receipt of all laboratory analytical data, Stone will prepare data tables and figures. Stone will also prepare a brief summary and transmit this information to VTDEC for their review. Stone will participate in a discussion about the results with VTDEC and any stakeholders and will discuss any proposed additional activities, if needed. This summary and discussion are proposed to accelerate the schedule for any supplemental Phase II activities that may be deemed required.

Stone will also prepare a Phase II ESA Report in accordance with §35-305 of the I-Rule and ASTM standards. The report will document field activities, include a summary of all analytical results obtained, provide an evaluation of the data, present an updated conceptual site model and sensitive receptor survey, identify any data gaps, and offer conclusions and recommendations. The report will include full laboratory reports, field notes, and appropriate tables and figures.

4.9. Project Timeline

Stone is prepared to initiate Site activities upon acceptance of this proposed scope of services. The project timeline is proposed in Table 5, below. Standard laboratory turn-around time is 5 days, with the exception for PFASs and dioxins, which are 10 – 15 business days.

Table 5: Project Timeline

Task	Exp. Duration	Exp. Start Date	Exp. Completion Date	Deliverable
Task 1 – Work Plan / SSQAPP				
Draft SSQAPP			May 29, 2019	Draft SSQAPP
Regulatory Review	30 days	May 30, 2019	June 28, 2019	
Final SSQAPP	2 days	July 1, 2019	July 2, 2019	Response to Comments memo, as needed Final SSQAPP
Task 2 – Dig Safe/ Site Visit	2 days	July 10, 2019		Dig Safe Ticket Number
Task 3 – Phase II Investigation Field Work	2 weeks	July 22, 2019	August 2, 2019	Field Notes, call with VT DEC
Analytical Turn-Around[1]	15 business days	August 5, 2019	August 23, 2019	Laboratory Reports
Present Summary of Results & Stakeholder Meeting	1 day	Week of August 26, 2019		
Task 3 -Data Evaluation and Reporting				
Draft Phase II ESA Report	2 weeks	August 26, 2019	September 6, 2019	Draft Phase II ESA Report
VT DEC Review	2 weeks	September 6, 2019	September 20, 2019	
Final Phase II ESA Report	1 week	September 20, 2019	September 27, 2019	Response to Comments memo, as needed. Final Phase II ESA Report

[1]Laboratory analysis for PFAS is 10-15 business days; dioxin is 15 business days; all other 10 business days

4.10. Cost

The anticipated Costs to perform the scope of services described above is summarized in Table 6, below. A detailed cost estimate is provided as Appendix B.

Table 6: Cost Estimate

	Task	Professional Services	Consultant	Expenses	Total
1	Task 1 - Work Plan, Project Coordination, HASP, Dig Safe & Monitoring Well Assessment & Redevelopment	$4,935	$1,144	$442	$6,521
2	Task 2 - Soil Assessment	$8,500	$23,406	$3,013	$34,919
3	Task 3 - Groundwater Assessment	$6,800	$16,880	$4,780	$28,459
4	Task 4 – Data Evaluation and Reporting	$6,320	$0	$0	$6,320
	TOTAL	**$26,555**	**$41,430**	**$8,235**	**$76,219**

5. Form E: Sampling Design

5.1. Existing Well Investigation/ Development and Dye Testing

During the DigSafe mark out Stone will attempt to locate monitoring wells identified on previous environmental reports, including those observed during a Site visit on January 25, 2019. The condition of located wells will be evaluated for usability for hydraulic monitoring and gauged for non-aqueous phase liquid (NAPL) (if present) using an oil-water interface probe. Stone will determine whether wells can be redeveloped and used to collect quality groundwater samples. Stone will complete an elevation survey of monitoring wells.

If necessary, monitoring well redevelopment will be completed using a Waterra Hydrolift pump and all purge water will be contained in 55-gallon drums pending groundwater monitoring results. Stone will again gauge depth to groundwater and LNAPL (if present) in each existing groundwater monitoring well located. Stone will also install a staff gauge in the Connecticut River adjacent to the Site to measure surface water elevation. If it is not feasible to install a staff gauge on the shoreline, Stone will attempt to utilize preexisting structures or markers on the shoreline for this purpose. Data collected will be used to estimate horizontal hydraulic gradients at the Site.

The floor drain in the maintenance area (Figures 4 and 5) will be dye tested to attempt to determine the discharge location, potentially the existing septic tanks and on-Site water treatment system. Available plans and drawings of the facility will be reviewed to aid in determining where to observe for the absence and presence of dye during the test.

5.2. Soil Assessment

5.2.1. Sub Surface Soil Borings

To assess the exterior portions of the Site for subsurface soil contamination, up to 12 soil borings will be advanced in areas of concern, as shown of Figures 4 and 5. Soil borings will be advanced using a Geoprobe 7822 DT and closed piston direct push tooling (Geoprobe MC5 or DT325) appropriate for the geological setting and investigation objectives. Soil borings at each location will be recovered continuously in 5-foot acetate sleeves to target depths, as summarized in Table 7. If early refusals are encountered, Stone will step the location aside by 3 feet and re-attempt the boring. Soils will be logged for color, grain size, moisture content, and visual and olfactory evidence of contamination. Stone will field-screen soils for VOCs using a PID equipped with a 11.7eV lamp from every 1-foot vertical interval or at depths that represent a transition between strata. The PID will be calibrated prior to the start of field activities using a 100-ppm isobutylene span gas. Actual sample depth will be determined in the field based on field screening readings, and visual and olfactory evidence of contamination. VOC samples will only be collected from soil borings if PID readings are 5 ppm greater than background ambient air. Soil boring and sample locations will be geographically positioned using a sub-meter GPS.

All sub surface soil samples will be collected in laboratory supplied bottleware and in accordance with Stone's SOPs. Soil samples will be placed in an ice-filled cooler and shipped under chain of custody protocols to

NELAP accredited Alpha's Westboro, Massachusetts laboratory for analysis. Samples collected for dioxins, PFAS and metals will be transported by Alpha to their NELAP accredited laboratory in Mansfield, Massachusetts for analysis. QA/QC samples will include field duplicates collected at a 5% frequency and 1 trip blank per sample shipment containing VOC or PFAS samples. Analytical methods for subsurface soil samples include the following EPA Methods:

- VOCs – 8260C;
- SVOCs – 8270D, and 8270D-SIM[2];
- Dioxins/ Furans – 8290A;
- PCBs – 8082A;
- PFAS – 537(M); and
- Metals (23 TAL and cyanide) – 6010D, 7471B, and 4500CN-CE

Table 7: Summary of Proposed Soil Borings

Investigation Point ID(s)	Number of Soil Borings	Associated REC(s)	Investigation Approach	Analytical Parameters
IP-02, IP-03, IP-07	3	1,2,3,4	Soil borings will be advanced to beneath the groundwater table. Soil samples will be collected at up to 2 depths per location.	VOCs[1], SVOCs, Metals
IP-05	1	3,4	Soil boring will be advanced to 25 feet below ground surface in the area of the surface water storm drain where cracked pavement was noted.	VOCs[1], SVOCs, Dioxins/ Furans, PCBs, PFAS, Metals
IP-06	1	13	Soil borings will be advanced to beneath the groundwater table. Soil samples will be collected at up to 2 depths per location.	VOCs[1], SVOCs, Dioxins/ Furans, PCBs, PFAS, Metals
IP-12, IP-13	2	10	Soil borings will be advanced to 10 feet below ground surface.	VOCs[1], SVOCs, Metals
IP-15	1	9	Soil boring will be advanced adjacent to the active leach field to a depth of 10 feet below ground surface.	VOCs[1], SVOCs, Metals
IP-18, IP-19, IP-20, IP-21	4	7	Soil borings will be advanced within the footprint of the 1989 'Active Fill Area' until native material is observed. As a contingency, if fill material includes large obstructions that makes probing unfeasible, an excavator will be mobilized to install test pits to investigate the nature and extent of fill. Samples are contingent on identification of materials other than clean construction debris (i.e. concrete, rebar, asphalt, and plastic).	VOCs[1], SVOCs, Dioxins/ Furans, PCBs, PFAS, Metals

[1]Contigent on results of PID screening.

[2] For benzo(a)pyrene, and dibenzo(a,h)anthracene only.

5.2.2. Surface Soil Assessment

To assess whether the presence of a 55-gallon drum (REC 6; IP-17, Figure 4) has resulted in a release to the environment, Stone will screen soils near the drum for the presence of VOCs using a PID equipped with a 10.6eV lamp. The PID will be calibrated prior to the start of field activities using a 100-ppm isobutylene span gas. Hand tooling will be used to remove turf at each sample location, if present. Hand tooling will then be used to collect soil from the 0.0-0.5 ft bgs interval. Soils will be logged for color, grain size, and moisture content. A VOC samples will only be collected if PID readings are 5 ppm greater than background ambient air, or if there is a visual or olfactory indication of a release.

To evaluate whether Site contaminants of concern have been released in the vicinity of the active septic system (REC 9; IP-14, Figure 4), Stone will inspect surface soil from an area of stressed vegetation to the southwest of the active leach field. Hand tooling will be used to remove turf, and then utilized to collect soil from the 0.0-0.5 ft bgs interval. Soils will be logged for color, grain size, moisture content, and field screened for the presence of VOCs using a calibrated PID. One discrete sample will be collected for analysis of VOCs, SVOCs, and metals. The VOC samples will only be collected if PID readings are 5 ppm greater than background ambient air.

To assess the outdoor equipment storage area (REC 5; IP-11, Figure 4), Stone will visually inspect the ground surface for evidence of leaks of oil and/or hydraulic fluid. Hand tooling will be used to remove turf at several locations and used to assess whether any identified leaks have impacted surface soils beyond the upper 6 inches. Soils will be logged for color, grain size, moisture content, and field screened for the presence of VOCs using a calibrated PID. Stone will collect up to three discrete soil samples for analysis of VOCs, SVOCs and PCBs. A VOC samples will only be collected if PID readings are 5 ppm greater than background ambient air, or if there is a visual or olfactory indication of a release.

To evaluate soil quality adjacent to the railroad line, Stone will complete surface soil assessments following an incremental sampling methodology (ISM) in two decision units (DUs) for REC 11. DUs are presented on Figure 4 and include:

- DU1: along the Site rail spur on the northern boundary of the Site.
- DU2: along the adjacent rail corridor on the northern boundary of the Site.

Each ISM sample will consist of soil from a minimum of 30-grid based increments. Hand tooling will be used to remove topsoil and vegetation at each ISM location, if present. Hand tooling will be used to remove topsoil and vegetation, and then utilized to collect soil from the 0.0-0.5 ft bgs interval at each increment location. Upon retrieval, soil will be logged for texture, color, and moisture content. This sampling procedure will be repeated at three locations (A, B, and C) per increment, following a randomized sampling strategy, in order to generate three replicates of the ISM sample.

To collect each ISM replicate, approximately 20 grams of soil will be collected from each increment and placed in dedicated aluminum trays. Separate aluminum trays will be used for each of the three replicates within each DU. Once all increments have been sampled and soil aliquots placed in the aluminum trays, soil will be mixed, subsampled, and placed in sample containers in accordance with Stone SOPs. Subsampling will be conducted by spreading the mixed soil to uniform thickness across the aluminum trays, dividing the trays into 30 equally sized grid squares, and placing approximately 1 gram of soil from each grid square into each sample container. In this manner, approximately 30 grams of soil will be collected, which is adequate for analysis. An electronic field balance will be used to ensure the proper

amount of soil is collected from each increment and from each subsample grid square. Duplication is inherent in ISM; therefore, field duplicates will not be collected. Stone will calculate the 95% upper confidence level of the arithmetic mean (UCL) for each contaminant of concern detected. Calculated 95% UCL values will represent the maximum contaminant concentrations that is expected to be encountered within each DU ninety-five percent of the time. Upon collection, samples will be analyzed for PAHs and herbicides.

All surface soil samples will be collected in laboratory supplied bottleware and in accordance with Stone's SOPs. Soil samples will be placed in an ice-filled cooler and shipped under chain of custody protocols to NELAP accredited Alpha's Westboro, Massachusetts laboratory for analysis. Samples collected for dioxins, PFAS and metals will be transported by Alpha to their NELAP accredited laboratory in Mansfield, Massachusetts for analysis. Quality assurance/ quality control (QA/QC) samples will include field duplicates collected at a 5% frequency and 1 trip blank per sample shipment containing VOC or PFAs samples. Soil boring and sample locations will be geographically positioned using a sub-meter. Analytical methods for surface soil samples include the following EPA Methods:

- VOCs – 8260C;
- SVOCs – 8270D and 8270D-SIM[3];
- PCBs – 8082A;
- Metals (23 TAL and cyanide) – 6010D, 7471B, and 4500CN-CE;
- PAHs – 8270D, and 8270D-SIM[3]; and
- Herbicides – 8151A

5.3. Groundwater Assessment

To assess whether past Site practices have adversely affected groundwater quality, Stone will collect groundwater samples at up to 11 locations. Groundwater sample will be collected using a screen point sampler (Geoprobe SP22 or equivalent) installed using direct push methods described above for soil borings in Section 5.2.1. Groundwater sample locations are shown graphically on Figures 4 and 5. Five of the soil boring and groundwater sampling locations will be co-located. Stone will also collect groundwater samples from two on-Site production wells (IP-9, IP-10; Figure 4). The SP22 system includes a variable length stainless steel well screen deployed within a standard macro-core drill string. Once an interval is selected based on the observation of saturated soils within the soil boring, the SP22 system is driven to the target interval and the well screen exposed by retracting the drive rod. Groundwater samples are summarized below, in Table 8. Upon installation, Stone will purge the drive point using dedicated high-density polyethylene (HDPE) tubing and a peristaltic pump. Physical and chemical field parameters (pH, specific conductance, temperature, dissolved oxygen [DO], and oxidation reduction potential [ORP]) will be measured using a calibrated multi-parameter meter and flow-through cell system. Turbidity will be measured using a standalone turbidity meter. The well will be purged until the following parameters have stabilized:

- pH ± 0.1 unit
- Specific Conductance ±3%
- ORP ± 10 mV

[3] For benzo(a)pyrene, and dibenzo(a,h)anthracene only.

- DO ± 10%, or 3 consecutive readings below 0.5 mg/L
- Temperature ± 3%
- Turbidity ± 10%, or 3 consecutive readings below 5.0 nephelometric turbidity units (NTU)

Following stabilization, samples will be collected in accordance with Stone SOPs. For metals analyses, an additional sample bottle will be filled at each location with field filter groundwater if turbidity exceeds 10 NTUs. Groundwater samples will be collected into laboratory supplied bottleware, placed in an ice-filled cooler, and shipped under chain of custody protocols to NELAP accredited Alpha's Westboro, Massachusetts laboratory for analysis. Samples collected for dioxins, PFAS and metals will be transported by Alpha to their NELAP accredited laboratory in Mansfield, Massachusetts for analysis. Quality assurance/ quality control (QA/QC) samples will include field duplicates collected at a 5% frequency, 1 trip blank per sample shipment containing VOC or PFAs samples, 1 field blank per day of PFAS sampling, and 1 equipment blank sampling from groundwater sampling equipment. Groundwater sample locations will be geographically positioned using a sub-meter GPS. Analytical methods for groundwater samples include the following EPA Methods:

- VOCs – 8260C;
- SVOCs – 8270D, and 8270D-SIM[4];
- Dioxins/ Furans – 8290A;
- PCBs – 8082A;
- PFAS – 537(M); and
- Metals (23 TAL and cyanide) – 6010D, 6020B[5], 7470A, and 9010C/9012B

Table 8: Summary of Proposed Groundwater Samples

Investigation Point ID(s)	Number of Locations	Associated REC(s)	Investigation Approach	Analytical Parameters
IP-02, IP-03, IP-07	3	1,2,3,4	A Geoprobe SP22 drive point sampler will be advanced until an interval is selected based on the observation of saturated soils within the soil boring.	VOCs, SVOCs, PFAS, Metals[1]
IP-01, IP-04,	2	3,4		VOCs, SVOCs, PFAS, Metals[1]
IP-05	1	3,4		VOCs, SVOCs, Dioxins/ Furans, PCBs, PFAS, Metals[1]
IP-06	1	13		VOCs, SVOCs, Dioxins/ Furans, PCBs, PFAS, Metals[1]
IP-08	1	13		VOCs, SVOCs, PFAS, Metals[1]

[4] For benzo(a)pyrene only.
[5] For arsenic, antimony, and thallium only.

Investigation Point ID(s)	Number of Locations	Associated REC(s)	Investigation Approach	Analytical Parameters
IP-09, IP-10	2	3,4	Groundwater samples will be collected from the two on-Site production wells.	VOCs, SVOCs, Metals[1]
IP-16	1	12	Locate, redevelop, and sample the formerly existing MW-9. If MW-9 cannot be located, a Geoprobe SP22 drive point sampler will be advanced until an interval is selected based on the observation of saturated soils within the soil boring.	VOCs, Metals[1]

[1]Metals will only be field filtered if turbidity exceeds 10 NTUs.

5.4. Wastewater Treatment Lagoon Sludge Assessment

To evaluate potential contaminants in the sludge generated in the wastewater treatment plant lagoons per VT DEC's request, Stone will collect one sample of the dried sludge from the on-Site stockpile. The single sample will be collected in laboratory supplied bottleware and in accordance with Stone's SOPs. The sludge sample will be placed in an ice-filled cooler and shipped under chain of custody protocols to NELAP accredited Alpha's Westboro, Massachusetts laboratory for analysis. Samples collected for dioxins, PFAS and metals will be transported by Alpha to their NELAP accredited laboratory in Mansfield, Massachusetts for analysis. Quality assurance/ quality control (QA/QC) samples will include a trip blank per sample shipment containing VOC or PFAS samples. Analytical methods for the lagoon sludge sample include the following EPA Methods:

- VOCs – 8260C;
- SVOCs – 8270D, and 8270D-SIM[6];
- Dioxins/ Furans – 8290A;
- PCBs – 8082A;
- PFAS – 537(M); and
- Metals (23 TAL and cyanide) – 6010D, 7471B, and 4500CN-CE

[6] For benzo(a)pyrene, and dibenzo(a,h)anthracene only.

6. Form F-1: Method and SOP Reference Table

Study-specific laboratory and Stone SOPs are listed in Tables 9 and 10 respectively and provided in Appendix D of the BA Generic QAPP. Alpha's SOPs summarized below in Table 9 were not included in the Ba Generic QAPP and are attached in Appendix C.

Table 9: Analytical Method Reference Table

Analytical Method Reference		Project Analytical SOPs	
SOP No. 2108.19	SOP No. 2108.19: Volatile Organic Compounds EPA 8260	SOP No. 2108.19	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No. 2111.21	SOP No. 2111.21: Semi-volatile Organics by GC/MS EPA 8270	SOP No. 2111.21	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No. 2109.11	SOP No. 2109.11: Polynuclear Aromatic Hydrocarbons (PAHs) by SIM EPA 8270 (M)	SOP No. 2109.11	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No. 25896.3	SOP No. 25896.3: EPA 8290A Dioxins and Furans by Hi-Res MS	SOP No. 25896.3	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No. 2129.9	SOP No. 2129.9: PCBs by Capillary Column GC EPA 8082	SOP No. 2129.9	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No. 29033.1	SOP No. 29033.1: PFAS by LC/MS/MS in Non-Potable Water	SOP No. 29033.1	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No. 23528.12	SOP No. 23528.12: PFAS by SPE and LC/MS/MS Isotope Dilution	SOP No. 23528.12	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No. 26796.2	SOP No. 26796.2: Metals by ICP EPA 6010D	SOP No. 26796.2	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No. 25923.1	SOP No. 25923.1: Mercury in Liquid Waste (Automated Cold-Vapor Technique) EPA 7470	SOP No. 25923.1	Alpha Analytical, Mansfield, Massachusetts
SOP No. 25924.1	SOP No.25924.1: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique) EPA 7471	SOP No. 25924.1	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No.2210.11	SOP No. 2210.11: Total and Amenable Cyanide	SOP No.2210.11	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No.26796.3	SOP No, 26796.3: Inductively Coupled Plasma – Mass Spectrometry 6020B	SOP No.26796.3	Alpha Analytical, Westboro & Mansfield, Massachusetts
SOP No. 2128.7	SOP No. 2128.7: Herbicides EPA 8151A	SOP No. 2128.7	Alpha Analytical, Westboro & Mansfield, Massachusetts

Table 10: Project Sampling Procedures Reference Table

Project Sampling SOPs*	
1b	SEI-SOP 5.1.5: Maintenance and Decontamination of Field Equipment
2b	SEI-SOP 5.34.5: Installation, Development and Decommissioning of Monitoring Wells and Observation Wells
6b	SEI-SOP 5.49.1: Procedure for Sampling Groundwater Monitoring Wells Using Low Stress (Low Flow) Technique
13b	SEI-5.56.2: Geologic Description of Unconsolidated Deposits Using the Wentworth Grain Size Scale
14b	SEI-5.58.1: Collection, Handling, and Preservation of Discrete Soil Samples
19b	SEI-5.63.0: Use, Maintenance and Calibration of the IonScience Tiger Photoionization Detector (PID)
24b	SEI-4.2.7: Chain of Custody Procedures
25b	SEI-4.5.12: Data Handling, Storage, Retrieval and Error Coding
27b	SEI-5.1.5: Maintenance and Decontamination of Field Equipment
31b	SEI-5.41.4: Handling, Collection and Transportation of Samples
SEI-5.94.0	SEI-5.94.0: Procedure for the Collection of Groundwater to be Analyzed for Per-and Polyfluoroalkyl Substances (PFAS)[1]

** Project Sampling SOPs include sample collection, sample preservation, equipment decontamination, preventive maintenance, etc.*

[1] - Stone SOP SEI-5.94.0: Procedure for the Collection of Groundwater to be Analyzed for Per-and Polyfluoroalkyl Substances (PFAS) was not included in the Generic BA QAPP and is attached to this SSQAPP in Appendix C

7. Form F-2: Sampling and Analytical Methods Requirements

Table 11: Sampling and Analytical Methods Requirements

Parameter	Matrix	Number of Samples	Field QC Samples	Analytical method[3]	Sampling SOP[4]	Containers per sample (number, size and type)	Preservation Requirements (temperature, light, chemical)	Maximum Holding Time at Lab from Collection (preparation/ analysis)
VOCs	Soil / Sludge	21[1,2]	1 FD 1 TB	SOP No. 2108.19	14b	2 – 40 mL VOA 40 mL % Solids	5 mL methanol Cool at ≤ 6°C	14 Days
	Groundwater	11	1 FD 3 TB		6b	3 – 40 mL VOA	HCl to pH ≤ 2 Cool at ≤ 6°C	14 Days
SVOCs	Soil / Sludge	20[2]	1 FD	SOP No. 2111.21, SOP No. 2109.11	14b	8-ounce glass jar	Cool at ≤ 6°C	14 Days
	Groundwater	10	1 FD		6b	2 – 250 mL amber jar	Cool at ≤ 6°C	7 Days
Dioxins / Furans	Soil / Sludge	7[2]	1 FD	SOP No. 25896.3	14b	8-ounce glass jar	Cool at ≤ 6°C	365 Days
	Groundwater	2	1 FD		6b	2 – 500 mL amber jar	Cool at ≤ 6°C	365 Days
PCB Aroclors	Soil / Sludge	10[2]	1 FD	SOP No. 2129.9	14b	8-ounce glass jar	Cool at ≤ 6°C	14 Days
	Groundwater	2	1 FD		6b	2 – 120 mL amber jar	Cool at ≤ 6°C	7 Days
PFAS	Soil / Sludge	7[2]	1 FD 1 TB	SOP No. 29033.1, SOP No. 23528.12	14b	8-ounce plastic jar	Cool at ≤ 6°C	28 Days
	Groundwater	8	1 FD 3 TB 1 EB 3 FB		SEI-5.94.0[5]	3 – 250 mL HDPE jar	5 g/L Trizma Cool at ≤ 6°C	14 Days

Parameter	Matrix	Number of Samples	Field QC Samples	Analytical method[3]	Sampling SOP[4]	Containers per sample (number, size and type)	Preservation Requirements (temperature, light, chemical)	Maximum Holding Time at Lab from Collection (preparation/ analysis)
Metals (23 TAL + cyanide)	Soil / Sludge	15[2]	1 FD	SOP No. 26796.2, SOP No. 25924.1, SOP No.2210.11	14b	8-ounce glass jar for Hg, 2 ounce glass jar all other metals	Cool at ≤ 6°C	28 days for Hg,14 days for CN, 180 days all other metals
	Groundwater	11[6]	1 FD	SOP No. 26796.2, SOP No.2210.11, SOP No. 25923.1, SOP No.26796.3	6b	250 mL poly for CN, 500 mL poly for all other metals	NaOH for CN, HNO3 to pH <2 for all other metals, Cool at ≤ 6°C	14 Days for CN, 28 days for Hg, 180 days all other metals
PAHs	Soil	6	1 FD	SOP No. 2111.21, SOP No. 2109.11	14b	8-ounce glass jar	Cool at ≤ 6°C	14 Days
Herbicides	Soil	6	1 FD	SOP No. 2128.7	14b	8-ounce glass jar	Cool at ≤ 6°C	14 Days

Abbreviations: FD – field duplicate; TB – trip blank; ° C – Degrees Celsius; Hg- Mercury
1 – Contingent on results of PID screening at in subsurface soil borings, and surface soil assessment at IP-17
2 – Contingent on identification of other than clean construction debris in IP-18 through IP-21. Full COC parameter list included in the event suspect waste sludge is identified in these 4 samples.
3 – Alpha's SOPs were not included in the Generic BA QAPP and are attached to this SSQAPP in Appendix C
4 – A list of Stone's sampling SOPs is provided in Table 3, Section 2.3 Page 21, of the Generic BA QAPP. Stone's sampling SOPs are provided as Appendix D of the Generic BA QAPP.
5 – Stone's SOP SEI-5.94.0 Procedure for the Collection of Groundwater to be Analyzed for Per-and Polyfluoroalkyl Substances (PFAS) was not included in the Generic BA QAPP and is attached to this SSQAPP in Appendix C.
6– Metals will only be field filtered if turbidity exceeds 10 NTUs.

8. Form G: Preventative Maintenance – Field Equipment

Preventive maintenance for field equipment is presented as Section 2.5.1 of the BA Generic QAPP. There are no changes for this Phase II ESA.

9. Form I: Preventative Maintenance – Laboratory Equipment

Preventive maintenance for laboratory equipment is presented as Section 2.5.2 of the BA Generic QAPP. There are no changes for this Phase II ESA.

10. Form J: Calibration and Corrective Action – Laboratory and Field Equipment

Calibration of instrumentation is required to ensure that the analytical system is operating correctly and functioning at the proper sensitivity to meet established reporting limits. Calibration and corrective actions for laboratory and field equipment are provided in Section 2.6 of the BA Generic QAPP. There are no updates for this Phase II ESA.

11. Form K: Sample Handling and Custody Requirements

Successful analysis depends on the capability to produce valid data and to demonstrate such validity. In addition to proper sample collection and handling, appropriate sample identification and chain of custody procedures are necessary to help support the validity of the data. These standard sample handling and custody requirements are described in detail in Section 2.2 of the BA Generic QAPP along with a typical chain of custody record. The sample handling and custody will be performed as described in the BA Generic QAPP and in accordance with Stone Standard Operating Procedures. Sample handling and custody at the receiving laboratory are described in the Laboratory Quality Manual, which can be made available upon request.

11.1. Site Sample Identification

Sample identifications will be presented as follows:

IP-##-DD.DD-QC

Where:

- IP is Investigation Point;
- DD.DD is Depth below ground surface in feet – soil borings only; and
- ## is the unique location identifier; and
- QC is quality control sample code (i.e., FD: Field Duplicate, TB: Trip Blank, EB: Equipment Blank, and FB: Field Blank)

Investigation point codes for this project will be as follows:

- SB: Soil Boring;
- SS: Surface Soil;
- SL: Sludge
- SP: Screen Point;
- MW: Monitoring well; and
- PW: Production Well.

Quality Assurance Codes for this project will be as follows:

- FD: Field Duplicate; and,
- TB: Trip Blank.

12. Form L: Analytical Precision and Accuracy

Table 12: Analytical Precision and Accuracy

Analyte	Matrix	Analytical Method*	Detection Limits	Quantitation Limits	Precision RPD	Accuracy %
VOCs	Soil	8260C	0.000108 - 0.0351 mg/ kg	0.0005 - 0.08 mg/kg	30	70-130
	Groundwater	8260C	0.0699 - 41.1 ug/l	0.5 - 250 ug/l	25	70-130
SVOCs/PAHS	Soil	8270D, 8270D-SIM	15.4642 - 181.028 ug/kg	100.2 - 801.6 ug/kg	50	30-140
	Groundwater	8270D, 8270D-SIM	0.257348 - 6.6612 ug/l	2.002 - 50.232 ug/l	30	30-140
Dioxins / Furans	Soil	8290A	0.0015 - 0.845 pg/g	0.0015 - 5 pg/g	25	66-144
	Groundwater	8290A	0.015 - 16.2 pg/l	0.015 - 50 pg/l	25	66-138
PCB Aroclors	Soil	8082A	0.0029748 - 0.007102 mg/kg	0.0335 - 0.0335 mg/kg	30	50-150
	Groundwater	8082A	0.0320586 - 0.0664734 ug/l	0.2499 - 0.299 ug/l	50	40-140
PFAS	Soil	537(M)	0.01035 - 3.81 ng/g	1 - 10 ng/g	30	50-150
	Groundwater	537(M)	0.564 – 1.632 ng/l	2 - 2 ng/l	30	70-130
Metals	Soil	6010D, 7471B, 4500CN-CE	0.0132 – 5.76 mg/kg	0.08 – 100 mg/kg	35 for CN, 20 for all other metals	75-125
	Groundwater	6010D, 6020B, 7470A, 9010C/9012B	0.0000915 – 0.237 mg/l	0.0002 – 2.5 mg/l	20	75-125
Herbicides	Soil	8181A	0.0044289 - 1.04895 mg/kg	0.0333 – 3.33 mg/kg	30	30-150

**Note: QA/QC limits in the laboratory may be more stringent and are reflected on the QA/QC summaries for that quality control sample.*

13. Form M: Field Quality Control Requirements

Table 13: Field Quality Control

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Field Duplicates	5% per analyte group	Precision 50% soil; 30% groundwater	Assess sampling precision, qualify data
VOA Trip Blank	1 per shipment containing VOC and PFAs samples	Accuracy/ Bias-contamination Target analytes < Quantitation Limit	Identify source of contamination during transit, qualify data
Field Blanks	1 per day of groundwater (PFAS only)	Accuracy/ Bias-contamination	Identify source of contamination, qualify data
Equipment Blank	1 groundwater equipment blank (PFAS only)	Accuracy/ Bias-contamination	Identify source of contamination, qualify data
Cooler Temperature	NA – temperature of the coolers should be taken upon receipt at the fixed laboratory.	4°C +/- 2°C	Report to client, if > 10°C, use professional judgement to continue with the analysis

14. Form M (Cont.): Laboratory Quality Control Requirements

Standard fixed laboratory quality control requirements as described in the method or Laboratory Quality Manuals are provided in Table 14. Control limits will vary from laboratory to laboratory; Form L provides the base standards.

Table 14: Laboratory Quality Control

QC Type	Frequency	Methodology	Acceptance Criteria	Corrective Action
method blank	1 per batch	Method blank subjected to same reagents and procedures as a field sample	Target analytes below RL	System check, reanalysis of affected samples
LCS	1 per batch	Reagent water or a blank matrix is spiked with a known concentration of analyte(s); purpose is to determine if possible MS/MSD failure was result of matrix issues or other procedural issues	Limits listed in method	Review, reanalyze LCS and associated samples, based on technical judgment.
MS/MSD	1 per matrix / 20 samples	Field sample is spiked with known concentration of analyte(s)	Limits listed in Method	Review LCS and recoveries. Report results in narrative regarding matrix affect.
ICV (independent)	After initial calibration	1 standard (ICP) or 3 standards (ICP-MS) or Internal standards 5-point average RF if <15% RSD or Linear reg. If >15% RSD (GC/MS)	% Recovery 70-130, unless otherwise listed in method	Review, reanalyze ICV, check standards, recalibrate if appropriate.
surrogate spike, organic analysis only	each sample, standard, blank		Limits listed in method	Review, reanalyze based on technical judgment

Notes: RL – Reporting Limit; LCS – Laboratory Controlled Spike, MS/MSD – Matrix Spike/Matrix Spike Duplicate, ICV – Initial Calibration Verification

15. Form N: Data Management and Documentation

Types of information to request from the laboratory:

- Project Narrative which contains all observation and deviations
- Data Results Sheets (include any performance evaluation sample results)
- Method Blank Results
- Surrogate Recoveries and Acceptance Limits
- Matrix Spike/Matrix Spike Duplicate Results and Acceptance Limits, if applicable
- Spike/Duplicate Results and Acceptance Limits
- Laboratory Control Sample Results and Acceptance Limits

Documentation requirements are described in Section 2.7 of the BA Generic QAPP. No changes are required for this Phase II ESA.

16. Forms O through R:

16.1. Form O: Assessment and Response Actions

Assessment and response actions are presented as Section 3.1 of the BA Generic QAPP. No updates are required for this Phase II ESA.

16.2. Form P: Project Reports

Requirements for project reports are described in Section 3.1.7 of the BA Generic QAPP. There are no changes for this Phase II ESA.

16.3. Form Q-1: Verification of Sampling Procedures

Requirements for verification of sampling procedures are described in Section 3 of the BA Generic QAPP. There are no changes for this Phase II ESA.

16.4. Form Q-2: Data Verification and Validation

Requirements for data verification and validation are described in Section 4 of the BA Generic QAPP. There are no changes for this Phase II ESA.

16.5. Form R: Data Usability

Requirements for data usability are presented in Section 4 of the BA Generic QAPP. There are no changes for this Phase II ESA.

Appendix A: Contaminants of Concern Tables

- Table A.1: VOCs in soil by EPA Method 8260C;
- Table A.2: VOCs in groundwater by EPA Method 8260C; and
- Table A.3: SVOCs and PAHs in soil by EPA Method 8270D, and 8270D-SIM for select analytes;
- Table A.4: SVOCs in groundwater by EPA Method 8270D, and 8270D-SIM for select analytes;
- Table A.5: Dioxins/ Furans in soil by EPA Method 8290A;
- Table A.6: Dioxins/ Furans in groundwater by EPA Method 8290A;
- Table A.7: PCBs in soil by EPA Method 8082A;
- Table A.8: PCBs in groundwater by EPA Method 8082A;
- Table A.9: PFAS in soil by EPA Method 537(M);
- Table A.10: PFAS in groundwater by EPA Method 537(M);
- Table A.11: Metals in soil by EPA Methods 6010D, 7471B, and 4500CN-CE;
- Table A.12: Metals in groundwater by EPA Methods 6010D, 6020B, 7470A, and 9010C/9012B;
- Table A.13: Herbicides in soil by EPA Method 8151A.

Table A.1: Site VOC Contaminants of Concern, Laboratory Quantitation Limits by EPA Method 8260C, and Action Limits - Soil

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	EPA Industrial Regional Screening Level (RSL)	EPA Residential Regional Screening Level (RSL)	Vermont Residential Screening Levels
630-20-6	1,1,1,2-Tetrachloroethane	0.000132	0.0005	mg/kg	8.8	2	NS
71-55-6	1,1,1-Trichloroethane	0.000167	0.0005	mg/kg	36000	8100	NS
79-34-5	1,1,2,2-Tetrachloroethane	0.000166	0.0005	mg/kg	2.7	0.6	NS
76-13-1	1,1,2-Trichloro-1,2,2-Trifluoroethane	0.000693	0.004	mg/kg	170000	40000	NS
79-00-5	1,1,2-Trichloroethane	0.000267	0.001	mg/kg	5	1.1	NS
75-34-3	1,1-Dichloroethane	0.000145	0.001	mg/kg	16	3.6	NS
75-35-4	1,1-Dichloroethene	0.000238	0.001	mg/kg	1000	230	NS
563-58-6	1,1-Dichloropropene	0.000159	0.0005	mg/kg	NS	NS	NS
87-61-6	1,2,3-Trichlorobenzene	0.000322	0.002	mg/kg	930	63	NS
96-18-4	1,2,3-Trichloropropane	0.000127	0.002	mg/kg	0.11	0.0051	0.00324
120-82-1	1,2,4-Trichlorobenzene	0.000272	0.002	mg/kg	110	24	NS
95-63-6	1,2,4-Trimethylbenzene	0.000334	0.002	mg/kg	240	58	NS
96-12-8	1,2-Dibromo-3-chloropropane	0.000998	0.003	mg/kg	0.064	0.0053	0.00327
106-93-4	1,2-Dibromoethane	0.000279	0.001	mg/kg	0.16	0.036	NS
95-50-1	1,2-Dichlorobenzene	0.000144	0.002	mg/kg	9300	1800	NS
107-06-2	1,2-Dichloroethane	0.000257	0.001	mg/kg	2	0.46	0.175
540-59-0	1,2-Dichloroethene (total)	0.000137	0.001	mg/kg	NS	NS	NS
78-87-5	1,2-Dichloropropane	0.000125	0.001	mg/kg	4.4	1	NS
108-70-3	1,3,5-Trichlorobenzene	0.000173	0.002	mg/kg	NS	NS	NS
108-67-8	1,3,5-Trimethylbenzene	0.000193	0.002	mg/kg	12000	780	NS
541-73-1	1,3-Dichlorobenzene	0.000148	0.002	mg/kg	NS	NS	NS
142-28-9	1,3-Dichloropropane	0.000167	0.002	mg/kg	23000	1600	NS
542-75-6	1,3-Dichloropropene, Total	0.000158	0.0005	mg/kg	8.2	1.8	NS
106-46-7	1,4-Dichlorobenzene	0.000171	0.002	mg/kg	11	2.6	NS
110-56-5	1,4-Dichlorobutane	0.000226	0.01	mg/kg	NS	NS	NS
123-91-1	1,4-Dioxane	0.0351	0.08	mg/kg	24	5.3	2.52
594-20-7	2,2-Dichloropropane	0.000202	0.002	mg/kg	NS	NS	NS
78-93-3	2-Butanone	0.00222	0.01	mg/kg	190000	27000	26000
591-78-6	2-Hexanone	0.00118	0.01	mg/kg	1300	200	NS
108-10-1	4-Methyl-2-pentanone	0.00128	0.01	mg/kg	140000	33000	NS
67-64-1	Acetone	0.004811	0.01	mg/kg	670000	61000	39900
107-13-1	Acrylonitrile	0.00115	0.004	mg/kg	1.1	0.25	NS
71-43-2	Benzene	0.000166	0.0005	mg/kg	5.1	1.2	0.442
108-86-1	Bromobenzene	0.000145	0.002	mg/kg	1800	290	NS
74-97-5	Bromochloromethane	0.000205	0.002	mg/kg	630	150	129
75-27-4	Bromodichloromethane	0.000109	0.0005	mg/kg	1.3	0.29	NS
75-25-2	Bromoform	0.000246	0.004	mg/kg	86	19	NS
74-83-9	Bromomethane	0.000581	0.002	mg/kg	30	6.8	NS
75-15-0	Carbon disulfide	0.00455	0.01	mg/kg	3500	770	NS
56-23-5	Carbon tetrachloride	0.00023	0.001	mg/kg	2.9	0.65	0.247
108-90-7	Chlorobenzene	0.000127	0.0005	mg/kg	1300	280	273
75-00-3	Chloroethane	0.000452	0.002	mg/kg	57000	14000	NS
67-66-3	Chloroform	0.00014	0.0015	mg/kg	1.4	0.32	NS
74-87-3	Chloromethane	0.000932	0.004	mg/kg	460	110	NS
156-59-2	cis-1,2-Dichloroethene	0.000175	0.001	mg/kg	2300	160	146
10061-01-5	cis-1,3-Dichloropropene	0.000158	0.0005	mg/kg	NS	NS	NS
110-82-7	Cyclohexane	0.000544	0.01	mg/kg	27000	6500	NS
124-48-1	Dibromochloromethane	0.00014	0.001	mg/kg	39	8.3	NS
74-95-3	Dibromomethane	0.000238	0.002	mg/kg	99	24	NS
75-71-8	Dichlorodifluoromethane	0.000915	0.01	mg/kg	370	87	NS
141-78-6	Ethyl Acetate	0.00121	0.01	mg/kg	2600	620	NS
60-29-7	Ethyl ether	0.000341	0.002	mg/kg	230000	16000	NS
97-63-2	Ethyl methacrylate	0.00158	0.01	mg/kg	7600	1800	NS
100-41-4	Ethylbenzene	0.000141	0.001	mg/kg	25	5.8	2.21
637-92-3	Ethyl-Tert-Butyl-Ether	0.000128	0.002	mg/kg	NS	NS	NS
87-68-3	Hexachlorobutadiene	0.000169	0.004	mg/kg	5.3	1.2	NS
108-20-3	Isopropyl Ether	0.000213	0.002	mg/kg	9400	2200	NS
98-82-8	Isopropylbenzene	0.000109	0.001	mg/kg	9900	1900	NS
79-20-9	Methyl Acetate	0.00095	0.004	mg/kg	1200000	78000	NS
108-87-2	Methyl cyclohexane	0.000603	0.004	mg/kg	NS	NS	NS
1634-04-4	Methyl tert butyl ether	0.000201	0.002	mg/kg	210	47	NS
75-09-2	Methylene chloride	0.00229	0.005	mg/kg	1000	57	NS
91-20-3	Naphthalene	0.00065	0.004	mg/kg	17	3.8	1.42
104-51-8	n-Butylbenzene	0.000167	0.001	mg/kg	58000	3900	NS
103-65-1	n-Propylbenzene	0.000171	0.001	mg/kg	24000	3800	NS
95-49-8	o-Chlorotoluene	0.000191	0.002	mg/kg	23000	1600	NS
95-47-6	o-Xylene	0.000291	0.001	mg/kg	2800	650	NS
179601-23-1	p/m-Xylene	0.00056	0.002	mg/kg	NS	NS	NS
106-43-4	p-Chlorotoluene	0.000108	0.002	mg/kg	23000	1600	NS
99-87-6	p-Isopropyltoluene	0.000109	0.001	mg/kg	NS	NS	NS
135-98-8	sec-Butylbenzene	0.000146	0.001	mg/kg	120000	7800	NS
100-42-5	Styrene	0.000196	0.001	mg/kg	35000	6000	NS
98-06-6	tert-Butylbenzene	0.000118	0.002	mg/kg	120000	7800	NS
994-05-8	Tertiary-Amyl Methyl Ether	0.000176	0.002	mg/kg	NS	NS	NS
127-18-4	Tetrachloroethene	0.000196	0.0005	mg/kg	100	24	1.46
109-99-9	Tetrahydrofuran	0.00159	0.004	mg/kg	94000	18000	NS
108-88-3	Toluene	0.000543	0.001	mg/kg	47000	4900	4640
156-60-5	trans-1,2-Dichloroethene	0.000137	0.0015	mg/kg	23000	1600	1460
10061-02-6	trans-1,3-Dichloropropene	0.000273	0.001	mg/kg	NS	NS	NS
110-57-6	trans-1,4-Dichloro-2-butene	0.00142	0.005	mg/kg	0.032	0.0074	NS
79-01-6	Trichloroethene	0.000137	0.0005	mg/kg	6	0.94	0.442
75-69-4	Trichlorofluoromethane	0.000695	0.004	mg/kg	350000	23000	NS
108-05-4	Vinyl acetate	0.00215	0.01	mg/kg	3800	910	NS
75-01-4	Vinyl chloride	0.000335	0.001	mg/kg	1.7	0.059	NS
1330-20-7	Xylene (Total)	0.000291	0.001	mg/kg	2500	580	575

NS: No standard for this compound; mg/kg: milligrams per kilogram

Table A.2: Site VOC Contaminants of Concern, Laboratory Quantitation Limits by EPA Method 8260C, and Action Limits - Groundwater

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	VGES
630-20-6	1,1,1,2-Tetrachloroethane	0.164	0.5	ug/l	70
71-55-6	1,1,1-Trichloroethane	0.158	0.5	ug/l	200
79-34-5	1,1,2,2-Tetrachloroethane	0.144	0.5	ug/l	NS
76-13-1	1,1,2-Trichloro-1,2,2-Trifluoroethane	0.148	10	ug/l	NS
79-00-5	1,1,2-Trichloroethane	0.144	0.75	ug/l	5
75-34-3	1,1-Dichloroethane	0.21	0.75	ug/l	70
75-35-4	1,1-Dichloroethene	0.142	0.5	ug/l	7
563-58-6	1,1-Dichloropropene	0.173	2.5	ug/l	NS
87-61-6	1,2,3-Trichlorobenzene	0.234	2.5	ug/l	NS
96-18-4	1,2,3-Trichloropropane	0.176	5	ug/l	5
95-93-2	1,2,4,5-Tetramethylbenzene	0.542	2	ug/l	NS
120-82-1	1,2,4-Trichlorobenzene	0.22	2.5	ug/l	70
95-63-6	1,2,4-Trimethylbenzene	0.191	2.5	ug/l	350
96-12-8	1,2-Dibromo-3-chloropropane	0.327	2.5	ug/l	NS
106-93-4	1,2-Dibromoethane	0.193	2	ug/l	NS
95-50-1	1,2-Dichlorobenzene	0.184	2.5	ug/l	600
107-06-2	1,2-Dichloroethane	0.132	0.5	ug/l	5
540-59-0	1,2-Dichloroethene (total)	0.163	0.5	ug/l	NS
78-87-5	1,2-Dichloropropane	0.133	1.75	ug/l	5
108-70-3	1,3,5-Trichlorobenzene	0.127	2	ug/l	40
108-67-8	1,3,5-Trimethylbenzene	0.174	2.5	ug/l	350
541-73-1	1,3-Dichlorobenzene	0.186	2.5	ug/l	600
142-28-9	1,3-Dichloropropane	0.212	2.5	ug/l	NS
542-75-6	1,3-Dichloropropene, Total	0.144	0.5	ug/l	NS
106-46-7	1,4-Dichlorobenzene	0.187	2.5	ug/l	75
110-56-5	1,4-Dichlorobutane	0.464	5	ug/l	NS
105-05-5	1,4-Diethylbenzene	0.392	2	ug/l	NS
123-91-1	1,4-Dioxane	41.1	250	ug/l	20
594-20-7	2,2-Dichloropropane	0.204	2.5	ug/l	NS
78-93-3	2-Butanone	1.94	5	ug/l	4200
591-78-6	2-Hexanone	0.515	5	ug/l	NS
622-96-8	4-Ethyltoluene	0.34	2	ug/l	NS
108-10-1	4-Methyl-2-pentanone	0.416	5	ug/l	560
67-64-1	Acetone	1.46	5	ug/l	700
107-13-1	Acrylonitrile	0.43	5	ug/l	NS
71-43-2	Benzene	0.159	0.5	ug/l	5
108-86-1	Bromobenzene	0.152	2.5	ug/l	NS
74-97-5	Bromochloromethane	0.138	2.5	ug/l	90
75-27-4	Bromodichloromethane	0.192	0.5	ug/l	80
75-25-2	Bromoform	0.248	2	ug/l	80
74-83-9	Bromomethane	0.256	1	ug/l	10
75-15-0	Carbon disulfide	0.299	5	ug/l	NS
56-23-5	Carbon tetrachloride	0.134	0.5	ug/l	5
108-90-7	Chlorobenzene	0.178	0.5	ug/l	100
75-00-3	Chloroethane	0.134	1	ug/l	NS
67-66-3	Chloroform	0.162	0.75	ug/l	80
74-87-3	Chloromethane	0.176	2.5	ug/l	30
156-59-2	cis-1,2-Dichloroethene	0.187	0.5	ug/l	70
10061-01-5	cis-1,3-Dichloropropene	0.144	0.5	ug/l	0.5
110-82-7	Cyclohexane	0.271	10	ug/l	NS
124-48-1	Dibromochloromethane	0.149	0.5	ug/l	80
74-95-3	Dibromomethane	0.363	5	ug/l	NS
75-71-8	Dichlorodifluoromethane	0.245	5	ug/l	1000
141-78-6	Ethyl Acetate	0.716	10	ug/l	NS
60-29-7	Ethyl ether	0.15	2.5	ug/l	NS
97-63-2	Ethyl methacrylate	0.606	5	ug/l	NS
100-41-4	Ethylbenzene	0.168	0.5	ug/l	700
637-92-3	Ethyl-Tert-Butyl-Ether	0.179	2	ug/l	NS
87-68-3	Hexachlorobutadiene	0.217	0.5	ug/l	1
108-20-3	Isopropyl Ether	0.425	2	ug/l	NS
98-82-8	Isopropylbenzene	0.187	0.5	ug/l	NS
79-20-9	Methyl Acetate	0.234	10	ug/l	NS
108-87-2	Methyl cyclohexane	0.396	10	ug/l	NS
1634-04-4	Methyl tert butyl ether	0.16	1	ug/l	40
75-09-2	Methylene chloride	0.289	3	ug/l	5
91-20-3	Naphthalene	0.216	2.5	ug/l	20
104-51-8	n-Butylbenzene	0.192	0.5	ug/l	NS
103-65-1	n-Propylbenzene	0.173	0.5	ug/l	NS
95-49-8	o-Chlorotoluene	0.17	2.5	ug/l	100
95-47-6	o-Xylene	0.33	1	ug/l	10000
179601-23-1	p/m-Xylene	0.332	1	ug/l	NS
106-43-4	p-Chlorotoluene	0.185	2.5	ug/l	100
99-87-6	p-Isopropyltoluene	0.188	0.5	ug/l	NS
135-98-8	sec-Butylbenzene	0.181	0.5	ug/l	NS
100-42-5	Styrene	0.359	1	ug/l	100
98-06-6	tert-Butylbenzene	0.185	2.5	ug/l	NS
994-05-8	Tertiary-Amyl Methyl Ether	0.278	2	ug/l	NS
127-18-4	Tetrachloroethene	0.181	0.5	ug/l	5
109-99-9	Tetrahydrofuran	0.525	5	ug/l	NS
108-88-3	Toluene	0.161	0.75	ug/l	1000
156-60-5	trans-1,2-Dichloroethene	0.163	0.75	ug/l	100
10061-02-6	trans-1,3-Dichloropropene	0.164	0.5	ug/l	0.5
110-57-6	trans-1,4-Dichloro-2-butene	0.173	2.5	ug/l	NS
79-01-6	Trichloroethene	0.175	0.5	ug/l	5
75-69-4	Trichlorofluoromethane	0.161	2.5	ug/l	2100
108-05-4	Vinyl acetate	0.311	5	ug/l	NS
75-01-4	Vinyl chloride	0.0699	1	ug/l	2
1330-20-7	Xylene (Total)	0.33	1	ug/l	10000

NS: No standard for this compound; ug/l: micrograms per liter

Table A.3: Site SVOC and PAH Contaminants of Concern, Laboratory Quantitation Limits by EPA Methods 8270D and 8270D-SIM, and Action Limits - Soil

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	EPA Industrial Regional Screening Level (RSL)	EPA Residential Regional Screening Level (RSL)	Vermont Residential Screening Levels
120-82-1	1,2,4-Trichlorobenzene	0.0191048	0.167	mg/kg	110	24	NS
95-50-1	1,2-Dichlorobenzene	0.0299932	0.167	mg/kg	9300	1800	NS
541-73-1	1,3-Dichlorobenzene	0.028724	0.167	mg/kg	NS	NS	NS
106-46-7	1,4-Dichlorobenzene	0.0291582	0.167	mg/kg	11	2.6	NS
90-12-0	1-Methylnaphthalene	0.019372	0.167	mg/kg	73	18	NS
95-95-4	2,4,5-Trichlorophenol	0.0319972	0.167	mg/kg	82000	6300	NS
88-06-2	2,4,6-Trichlorophenol	0.0316632	0.1002	mg/kg	210	49	NS
120-83-2	2,4-Dichlorophenol	0.0268536	0.1503	mg/kg	2500	190	NS
105-67-9	2,4-Dimethylphenol	0.05511	0.167	mg/kg	16000	1300	NS
51-28-5	2,4-Dinitrophenol	0.077822	0.8016	mg/kg	1600	130	NS
121-14-2	2,4-Dinitrotoluene	0.0334	0.167	mg/kg	7.4	1.7	NS
606-20-2	2,6-Dinitrotoluene	0.0286572	0.167	mg/kg	1.5	0.36	NS
91-58-7	2-Chloronaphthalene	0.0165664	0.167	mg/kg	60000	4800	NS
95-57-8	2-Chlorophenol	0.0197394	0.167	mg/kg	5800	390	NS
91-57-6	2-Methylnaphthalene	0.0201736	0.2004	mg/kg	3000	240	NS
95-48-7	2-Methylphenol	0.025885	0.167	mg/kg	41000	3200	NS
88-74-4	2-Nitroaniline	0.0321976	0.167	mg/kg	8000	630	NS
88-75-5	2-Nitrophenol	0.062792	0.36072	mg/kg	NS	NS	NS
91-94-1	3,3'-Dichlorobenzidine	0.044422	0.167	mg/kg	5.1	1.2	NS
108-39-4/106-44-5	3-Methylphenol/4-Methylphenol	0.0261522	0.24048	mg/kg	NS	NS	NS
99-09-2	3-Nitroaniline	0.0314962	0.167	mg/kg	NS	NS	NS
534-52-1	4,6-Dinitro-o-cresol	0.08016	0.4342	mg/kg	66	5.1	NS
101-55-3	4-Bromophenyl phenyl ether	0.0254842	0.167	mg/kg	NS	NS	NS
106-47-8	4-Chloroaniline	0.030394	0.167	mg/kg	11	2.7	NS
7005-72-3	4-Chlorophenyl phenyl ether	0.017869	0.167	mg/kg	NS	NS	NS
100-01-6	4-Nitroaniline	0.069138	0.167	mg/kg	110	27	NS
100-02-7	4-Nitrophenol	0.068136	0.2338	mg/kg	NS	NS	NS
83-32-9	Acenaphthene	0.0173012	0.1336	mg/kg	45000	3600	NS
208-96-8	Acenaphthylene	0.0257848	0.1336	mg/kg	NS	NS	NS
62-53-3	Aniline	0.078824	0.2004	mg/kg	400	95	NS
120-12-7	Anthracene	0.032565	0.1002	mg/kg	230000	18000	NS
103-33-3	Azobenzene	0.016032	0.167	mg/kg	26	5.6	NS
92-87-5	Benzidine	0.181028	0.5511	mg/kg	0.01	0.00053	NS
56-55-3	Benzo(a)anthracene	0.0188042	0.1002	mg/kg	2.9	0.16	NS
50-32-8	Benzo(a)pyrene	0.0006346	0.0068	mg/kg	0.29	0.016	0.076
205-99-2	Benzo(b)fluoranthene	0.0281228	0.1002	mg/kg	2.9	0.16	NS
191-24-2	Benzo(ghi)perylene	0.0196392	0.1336	mg/kg	NS	NS	NS
207-08-9	Benzo(k)fluoranthene	0.02672	0.1002	mg/kg	29	1.6	NS
65-85-0	Benzoic Acid	0.169004	0.54108	mg/kg	3300000	250000	NS
100-51-6	Benzyl Alcohol	0.051102	0.167	mg/kg	82000	6300	NS
92-52-4	Biphenyl	0.038744	0.38076	mg/kg	200	47	NS
111-91-1	Bis(2-chloroethoxy)methane	0.0167334	0.18036	mg/kg	2500	190	NS
111-44-4	Bis(2-chloroethyl)ether	0.0226452	0.1503	mg/kg	1	0.23	NS
108-60-1	Bis(2-chloroisopropyl)ether	0.0285236	0.2004	mg/kg	47000	3100	2920
117-81-7	Bis(2-Ethylhexyl)phthalate	0.057782	0.167	mg/kg	160	39	20.7
85-68-7	Butyl benzyl phthalate	0.042084	0.167	mg/kg	1200	290	NS
86-74-8	Carbazole	0.0162324	0.167	mg/kg	NS	NS	NS
218-01-9	Chrysene	0.017368	0.1002	mg/kg	290	16	NS
53-70-3	Dibenzo(a,h)anthracene	0.000668	0.00668	mg/kg	0.29	0.016	NS
132-64-9	Dibenzofuran	0.0157982	0.167	mg/kg	1000	73	NS
84-66-2	Diethyl phthalate	0.0154642	0.167	mg/kg	660000	51000	NS
131-11-3	Dimethyl phthalate	0.03507	0.167	mg/kg	NS	NS	NS
84-74-2	Di-n-butylphthalate	0.0316632	0.167	mg/kg	82000	6300	NS
117-84-0	Di-n-octylphthalate	0.05678	0.167	mg/kg	8200	630	NS
206-44-0	Fluoranthene	0.0191716	0.1002	mg/kg	30000	2400	NS
86-73-7	Fluorene	0.0162324	0.167	mg/kg	30000	2400	NS
118-74-1	Hexachlorobenzene	0.018704	0.1002	mg/kg	0.96	0.21	0.0918
87-68-3	Hexachlorobutadiene	0.0244488	0.167	mg/kg	5.3	1.2	NS
77-47-4	Hexachlorocyclopentadiene	0.151302	0.47762	mg/kg	7.5	1.8	NS
67-72-1	Hexachloroethane	0.0270206	0.1336	mg/kg	8	1.8	NS
193-39-5	Indeno(1,2,3-cd)Pyrene	0.0232798	0.1336	mg/kg	2.9	0.16	NS
78-59-1	Isophorone	0.0216766	0.1503	mg/kg	2400	570	NS
91-20-3	Naphthalene	0.0203406	0.167	mg/kg	17	3.8	1.42
98-95-3	Nitrobenzene	0.024716	0.1503	mg/kg	22	5.1	NS
86-30-6	NitrosoDiPhenylAmine(NDPA)/DPA	0.0190046	0.1336	mg/kg	470	110	NS
62-75-9	n-Nitrosodimethylamine	0.032064	0.334	mg/kg	0.034	0.002	NS
621-64-7	n-Nitrosodi-n-propylamine	0.0257848	0.167	mg/kg	0.33	0.078	NS
59-50-7	P-Chloro-M-Cresol	0.024883	0.167	mg/kg	82000	6300	NS
87-86-5	Pentachlorophenol	0.03674	0.1336	mg/kg	4	1	0.504
85-01-8	Phenanthrene	0.0203072	0.1002	mg/kg	NS	NS	NS
108-95-2	Phenol	0.025217	0.167	mg/kg	250000	19000	NS
129-00-0	Pyrene	0.0165998	0.1002	mg/kg	23000	1800	NS
110-86-1	Pyridine	0.06346	0.18036	mg/kg	1200	78	NS

NS: No standard for this compound; mg/kg: milligrams per kilogram

Table A.4: Site SVOC Contaminants of Concern, Laboratory Quantitation Limits by EPA Methods 8270D and 8270D-SIM, and Action Limits - Groundwater

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	VGES
120-82-1	1,2,4-Trichlorobenzene	0.49868	5.0232	ug/l	70
95-50-1	1,2-Dichlorobenzene	0.455	2.002	ug/l	600
541-73-1	1,3-Dichlorobenzene	0.40404	2.002	ug/l	600
106-46-7	1,4-Dichlorobenzene	0.43316	2.002	ug/l	75
90-12-0	1-Methylnaphthalene	0.44772	2.002	ug/l	NS
95-95-4	2,4,5-Trichlorophenol	0.77532	5.0232	ug/l	NS
88-06-2	2,4,6-Trichlorophenol	0.61152	5.0232	ug/l	NS
120-83-2	2,4-Dichlorophenol	0.41132	5.0232	ug/l	NS
105-67-9	2,4-Dimethylphenol	1.77996	5.0232	ug/l	NS
51-28-5	2,4-Dinitrophenol	6.6612	20.02	ug/l	NS
121-14-2	2,4-Dinitrotoluene	1.1648	5.0232	ug/l	NS
606-20-2	2,6-Dinitrotoluene	0.93184	5.0232	ug/l	NS
91-58-7	2-Chloronaphthalene	0.4368	2.002	ug/l	NS
95-57-8	2-Chlorophenol	0.48048	2.002	ug/l	NS
91-57-6	2-Methylnaphthalene	0.455	2.002	ug/l	NS
95-48-7	2-Methylphenol	0.4914	5.0232	ug/l	NS
88-74-4	2-Nitroaniline	0.49868	5.0232	ug/l	NS
88-75-5	2-Nitrophenol	0.84812	10.01	ug/l	NS
91-94-1	3,3'-Dichlorobenzidine	1.62344	5.0232	ug/l	NS
108-39-4/106-44-5	3-Methylphenol/4-Methylphenol	0.48048	5.0232	ug/l	NS
99-09-2	3-Nitroaniline	0.81536	5.0232	ug/l	NS
534-52-1	4,6-Dinitro-o-cresol	1.81636	10.01	ug/l	NS
101-55-3	4-Bromophenyl phenyl ether	0.37856	2.002	ug/l	NS
106-47-8	4-Chloroaniline	1.07016	5.0232	ug/l	NS
7005-72-3	4-Chlorophenyl phenyl ether	0.48776	2.002	ug/l	NS
100-01-6	4-Nitroaniline	0.8008	5.0232	ug/l	NS
100-02-7	4-Nitrophenol	0.6734	10.01	ug/l	NS
83-32-9	Acenaphthene	0.44408	2.002	ug/l	NS
208-96-8	Acenaphthylene	0.46592	2.002	ug/l	NS
62-53-3	Aniline	0.67704	2.002	ug/l	NS
120-12-7	Anthracene	0.32942	2.002	ug/l	2100
103-33-3	Azobenzene	0.36764	2.002	ug/l	NS
92-87-5	Benzidine	1.79816	20.02	ug/l	NS
56-55-3	Benzo(a)anthracene	0.32578	2.002	ug/l	NS
50-32-8	Benzo(a)pyrene	0.01493856	0.1001	ug/l	0.2
205-99-2	Benzo(b)fluoranthene	0.355264	2.002	ug/l	NS
191-24-2	Benzo(ghi)perylene	0.296296	2.002	ug/l	NS
207-08-9	Benzo(k)fluoranthene	0.37492	2.002	ug/l	NS
65-85-0	Benzoic Acid	2.66084	50.232	ug/l	NS
100-51-6	Benzyl Alcohol	0.58968	2.002	ug/l	NS
92-52-4	Biphenyl	0.45864	2.002	ug/l	NS
111-91-1	Bis(2-chloroethoxy)methane	0.50232	5.0232	ug/l	NS
111-44-4	Bis(2-chloroethyl)ether	0.50596	2.002	ug/l	NS
108-60-1	Bis(2-chloroisopropyl)ether	0.5278	2.002	ug/l	NS
117-81-7	Bis(2-Ethylhexyl)phthalate	1.53608	3.003	ug/l	NS
85-68-7	Butyl benzyl phthalate	1.17208	5.0232	ug/l	NS
86-74-8	Carbazole	0.4914	2.002	ug/l	NS
218-01-9	Chrysene	0.341068	2.002	ug/l	NS
53-70-3	Dibenzo(a,h)anthracene	0.323232	2.002	ug/l	NS
132-64-9	Dibenzofuran	0.49868	2.002	ug/l	NS
84-66-2	Diethyl phthalate	0.3822	5.0232	ug/l	NS
131-11-3	Dimethyl phthalate	1.82	5.0232	ug/l	NS
84-74-2	Di-n-butylphthalate	0.38948	5.0232	ug/l	NS
117-84-0	Di-n-octylphthalate	1.274	5.0232	ug/l	NS
206-44-0	Fluoranthene	0.257348	2.002	ug/l	280
86-73-7	Fluorene	0.41496	2.002	ug/l	NS
118-74-1	Hexachlorobenzene	0.46592	2.002	ug/l	NS
87-68-3	Hexachlorobutadiene	0.65884	2.002	ug/l	1
77-47-4	Hexachlorocyclopentadiene	0.68796	20.02	ug/l	NS
67-72-1	Hexachloroethane	0.58604	2.002	ug/l	NS
193-39-5	Indeno(1,2,3-cd)Pyrene	0.39676	2.002	ug/l	NS
78-59-1	Isophorone	1.20484	5.0232	ug/l	NS
91-20-3	Naphthalene	0.46592	2.002	ug/l	20
98-95-3	Nitrobenzene	0.77168	2.002	ug/l	NS
86-30-6	NitrosoDiPhenylAmine(NDPA)/DPA	0.4186	2.002	ug/l	NS
62-75-9	n-Nitrosodimethylamine	0.75712	2.002	ug/l	NS
621-64-7	n-Nitrosodi-n-propylamine	0.64428	5.0232	ug/l	NS
59-50-7	P-Chloro-M-Cresol	0.35126	2.002	ug/l	NS
87-86-5	Pentachlorophenol	1.79452	10.01	ug/l	NS
85-01-8	Phenanthrene	0.33124	2.002	ug/l	NS
108-95-2	Phenol	0.56784	5.0232	ug/l	NS
129-00-0	Pyrene	0.279552	2.002	ug/l	NS
110-86-1	Pyridine	1.76904	3.50532	ug/l	NS

NS: No standard for this compound; ug/l: micrograms per liter

Table A.5: Site Dioxins and Furans Contaminants of Concern, Laboratory Quantitation Limits by EPA Method 8290A, and Action Limits - Soil

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	EPA Industrial Regional Screening Level (RSL)	EPA Residential Regional Screening Level (RSL)	Vermont Residential Screening Levels
35822-46-9	1,2,3,4,6,7,8-HpCDD	0.000000271	0.0000025	mg/kg	NS	NS	NS
67562-39-4	1,2,3,4,6,7,8-HpCDF	0.000000396	0.0000025	mg/kg	NS	NS	NS
55673-89-7	1,2,3,4,7,8,9-HpCDF	0.000000274	0.0000025	mg/kg	NS	NS	NS
39227-28-6	1,2,3,4,7,8-HxCDD	0.000000552	0.0000025	mg/kg	NS	NS	NS
70648-26-9	1,2,3,4,7,8-HxCDF	0.00000032	0.0000025	mg/kg	NS	NS	NS
57653-85-7	1,2,3,6,7,8-HxCDD	0.000000429	0.0000025	mg/kg	NS	NS	NS
57117-44-9	1,2,3,6,7,8-HxCDF	0.00000035	0.0000025	mg/kg	NS	NS	NS
19408-74-3	1,2,3,7,8,9-HxCDD	0.000000383	0.0000025	mg/kg	NS	NS	NS
72918-21-9	1,2,3,7,8,9-HxCDF	0.000000284	0.0000025	mg/kg	NS	NS	NS
40321-76-4	1,2,3,7,8-PeCDD	0.000000367	0.0000025	mg/kg	NS	NS	NS
57117-41-6	1,2,3,7,8-PeCDF	0.0000003	0.0000025	mg/kg	NS	NS	NS
60851-34-5	2,3,4,6,7,8-HxCDF	0.000000304	0.0000025	mg/kg	NS	NS	NS
57117-31-4	2,3,4,7,8-PeCDF	0.000000251	0.0000025	mg/kg	NS	NS	NS
1746-01-6	2,3,7,8-TCDD	0.000000154	0.0000005	mg/kg	0.000022	0.0000048	0.00000233
51207-31-9	2,3,7,8-TCDF	0.000000138	0.0000005	mg/kg	NS	NS	NS
3268-87-9	OCDD	0.00000053	0.000005	mg/kg	NS	NS	NS
39001-02-0	OCDF	0.000000845	0.000005	mg/kg	NS	NS	NS
	TEQ	0.0000000015	0.0000000015	mg/kg	NS	NS	NS
37871-00-4	Total HpCDD	0.000000271	0.0000025	mg/kg	NS	NS	NS
38998-75-3	Total HpCDF	0.000000396	0.0000025	mg/kg	NS	NS	NS
34465-46-8	Total HxCDD	0.000000552	0.0000025	mg/kg	NS	NS	NS
55684-94-1	Total HxCDF	0.00000032	0.0000025	mg/kg	NS	NS	NS
	Total PCDD	0.000000154	0.0000005	mg/kg	NS	NS	NS
	Total PCDF	0.000000138	0.0000005	mg/kg	NS	NS	NS
36088-22-9	Total PeCDD	0.000000367	0.0000025	mg/kg	NS	NS	NS
30402-15-4	Total PeCDF	0.0000003	0.0000025	mg/kg	NS	NS	NS
41903-57-5	Total TCDD	0.000000154	0.0000005	mg/kg	NS	NS	NS
55722-27-5	Total TCDF	0.000000138	0.0000005	mg/kg	NS	NS	NS

NS: No standard for this compound; mg/kg: milligrams per kilogram

Table A.6: Site Dioxins and Furans Contaminants of Concern, Laboratory Quantitation Limits by EPA Method 8290A, and Action Limits - Groundwater

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	VGES
35822-46-9	1,2,3,4,6,7,8-HpCDD	7.25	25	pg/l	NS
67562-39-4	1,2,3,4,6,7,8-HpCDF	6.71	25	pg/l	NS
55673-89-7	1,2,3,4,7,8,9-HpCDF	6.36	25	pg/l	NS
39227-28-6	1,2,3,4,7,8-HxCDD	6.27	25	pg/l	NS
70648-26-9	1,2,3,4,7,8-HxCDF	5.56	25	pg/l	NS
57653-85-7	1,2,3,6,7,8-HxCDD	7.78	25	pg/l	NS
57117-44-9	1,2,3,6,7,8-HxCDF	7.96	25	pg/l	NS
19408-74-3	1,2,3,7,8,9-HxCDD	7.3	25	pg/l	NS
72918-21-9	1,2,3,7,8,9-HxCDF	8.23	25	pg/l	NS
40321-76-4	1,2,3,7,8-PeCDD	5.19	25	pg/l	NS
57117-41-6	1,2,3,7,8-PeCDF	3.5	25	pg/l	NS
60851-34-5	2,3,4,6,7,8-HxCDF	7.92	25	pg/l	NS
57117-31-4	2,3,4,7,8-PeCDF	5.23	25	pg/l	NS
1746-01-6	2,3,7,8-TCDD	1.04	5	pg/l	NS
51207-31-9	2,3,7,8-TCDF	1.53	5	pg/l	NS
3268-87-9	OCDD	12.7	50	pg/l	NS
39001-02-0	OCDF	16.2	50	pg/l	NS
	TEQ	0.015	0.015	pg/l	NS
37871-00-4	Total HpCDD	7.25	25	pg/l	NS
38998-75-3	Total HpCDF	6.71	25	pg/l	NS
34465-46-8	Total HxCDD	6.27	25	pg/l	NS
55684-94-1	Total HxCDF	5.56	25	pg/l	NS
	Total PCDD	1.04	5	pg/l	NS
	Total PCDF	1.53	5	pg/l	NS
36088-22-9	Total PeCDD	5.19	25	pg/l	NS
30402-15-4	Total PeCDF	3.5	25	pg/l	NS
41903-57-5	Total TCDD	1.04	5	pg/l	NS
55722-27-5	Total TCDF	1.53	5	pg/l	NS

NS: No standard for this compound; pg/l: picograms per liter

Table A.7: Site PCB Contaminants of Concern, Laboratory Quantitation Limits by EPA Method 8082A, and Action Limits - Soil

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	EPA Industrial Regional Screening Level (RSL)	EPA Residential Regional Screening Level (RSL)	Vermont Residential Screening Levels
12674-11-2	Aroclor 1016	0.0029748	0.0335	mg/kg	27	4.1	NS
11104-28-2	Aroclor 1221	0.0033567	0.0335	mg/kg	0.83	0.2	NS
11141-16-5	Aroclor 1232	0.007102	0.0335	mg/kg	0.72	0.17	NS
53469-21-9	Aroclor 1242	0.0045158	0.0335	mg/kg	0.95	0.23	NS
12672-29-6	Aroclor 1248	0.005025	0.0335	mg/kg	0.95	0.23	NS
11097-69-1	Aroclor 1254	0.0036649	0.0335	mg/kg	0.97	0.24	0.12
11096-82-5	Aroclor 1260	0.0061908	0.0335	mg/kg	0.99	0.24	NS
37324-23-5	Aroclor 1262	0.0042545	0.0335	mg/kg	NS	NS	NS
11100-14-4	Aroclor 1268	0.0034706	0.0335	mg/kg	NS	NS	NS
1336-36-3	PCBs, Total	0.0029748	0.0335	mg/kg	0.94	0.23	0.114

NS: No standard for this compound; mg/kg: milligrams per kilogram

Table A.8: Site PCB Contaminants of Concern, Laboratory Quantitation Limits by EPA Method 8082A, and Action Limits - Groundwater

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	VGES
12674-11-2	Aroclor 1016	0.0344148	0.2499	ug/l	0.5
11104-28-2	Aroclor 1221	0.0664734	0.2499	ug/l	0.5
11141-16-5	Aroclor 1232	0.0455532	0.2499	ug/l	0.5
53469-21-9	Aroclor 1242	0.0387702	0.2499	ug/l	0.5
12672-29-6	Aroclor 1248	0.048909	0.2499	ug/l	0.5
11097-69-1	Aroclor 1254	0.0390558	0.2499	ug/l	0.5
11096-82-5	Aroclor 1260	0.0320586	0.2499	ug/l	0.5
37324-23-5	Aroclor 1262	0.0347718	0.2499	ug/l	NS
11100-14-4	Aroclor 1268	0.0334866	0.2499	ug/l	NS
1336-36-3	PCBs, Total	0.0320586	0.2499	ug/l	NS

ug/l: micrograms per liter

Table A.9: Site PFAS Contaminants of Concern, Laboratory Quantitation Limits by EPA Method 537(M), and Action Limits - Soil

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	EPA Industrial Regional Screening Level (RSL)	EPA Residential Regional Screening Level (RSL)	Vermont Residential Screening Levels
39108-34-4	1H,1H,2H,2H-Perfluorodecanesulfonic Acid (8:2FTS)	0.000275	0.001	mg/kg	NS	NS	NS
	1H,1H,2H,2H-Perfluorohexanesulfonic Acid (4:2FTS)	0.000108	0.001	mg/kg	NS	NS	NS
27619-97-2	1H,1H,2H,2H-Perfluorooctanesulfonic Acid (6:2FTS)	0.000198	0.001	mg/kg	NS	NS	NS
13252-13-6	2,3,3,3-Tetrafluoro-2-[1,1,2,2,3,3,3-Heptafluoropropoxy]-Propanoic Acid (HFPO-DA)	0.00381	0.01	mg/kg	NS	NS	NS
919005-14-4	4,8-Dioxa-3h-Perfluorononanoic Acid (ADONA)	0.0000575	0.001	mg/kg	NS	NS	NS
2991-50-6	N-Ethyl Perfluorooctanesulfonamidoacetic Acid (NEtFOSAA)	0.00009	0.001	mg/kg	NS	NS	NS
2355-31-9	N-Methyl Perfluorooctanesulfonamidoacetic Acid (NMeFOSAA)	0.000103	0.001	mg/kg	NS	NS	NS
375-73-5	Perfluorobutanesulfonic Acid (PFBS)	0.0000635	0.001	mg/kg	23000	1600	NS
375-22-4	Perfluorobutanoic Acid (PFBA)	0.0000213	0.001	mg/kg	NS	NS	NS
335-77-3	Perfluorodecanesulfonic Acid (PFDS)	0.000097	0.001	mg/kg	NS	NS	NS
335-76-2	Perfluorodecanoic Acid (PFDA)	0.000072	0.001	mg/kg	NS	NS	NS
307-55-1	Perfluorododecanoic Acid (PFDoA)	0.000086	0.001	mg/kg	NS	NS	NS
375-92-8	Perfluoroheptanesulfonic Acid (PFHpS)	0.000136	0.001	mg/kg	NS	NS	NS
375-85-9	Perfluoroheptanoic Acid (PFHpA)	0.000064	0.001	mg/kg	NS	NS	NS
67905-19-5	Perfluorohexadecanoic Acid (PFHxDA)	0.00012	0.001	mg/kg	NS	NS	NS
355-46-4	Perfluorohexanesulfonic Acid (PFHxS)	0.000057	0.001	mg/kg	NS	NS	NS
307-24-4	Perfluorohexanoic Acid (PFHxA)	0.000064	0.001	mg/kg	NS	NS	NS
68259-12-1	Perfluorononanesulfonic Acid (PFNS)	0.000088	0.001	mg/kg	NS	NS	NS
375-95-1	Perfluorononanoic Acid (PFNA)	0.000083	0.001	mg/kg	NS	NS	NS
16517-11-6	Perfluorooctadecanoic Acid (PFODA)	0.000171	0.001	mg/kg	NS	NS	NS
754-91-6	Perfluorooctanesulfonamide (FOSA)	0.0001025	0.001	mg/kg	NS	NS	NS
1763-23-1	Perfluorooctanesulfonic Acid (PFOS)	0.0001205	0.001	mg/kg	NS	NS	NS
335-67-1	Perfluorooctanoic Acid (PFOA)	0.00004105	0.001	mg/kg	NS	NS	0.3
2706-91-4	Perfluoropentanesulfonic Acid (PFPeS)	0.0000965	0.001	mg/kg	NS	NS	NS
2706-90-3	Perfluoropentanoic Acid (PFPeA)	0.00001035	0.001	mg/kg	NS	NS	NS
376-06-7	Perfluorotetradecanoic Acid (PFTA)	0.00007	0.001	mg/kg	NS	NS	NS
72629-94-8	Perfluorotridecanoic Acid (PFTrDA)	0.000062	0.001	mg/kg	NS	NS	NS
2058-94-8	Perfluoroundecanoic Acid (PFUnA)	0.000056	0.001	mg/kg	NS	NS	NS
	PFAS, Total (5)	0.00004105	0.001	mg/kg	NS	NS	NS
	PFOA/PFOS, Total	0.00004105	0.001	mg/kg	NS	NS	NS

NS: No standard for this compound; mg/kg: milligrams per kilogram

Table A.10: Site PFAS Contaminants of Concern, Laboratory Quantitation Limits by EPA Method 537(M), and Action Limits - Groundwater

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	VGES
2991-50-6	N-Ethyl Perfluorooctanesulfonamidoacetic Acid (NEtFOSAA)	0.596	2	ng/L	NS
2355-31-9	N-Methyl Perfluorooctanesulfonamidoacetic Acid (NMeFOSAA)	0.636	2	ng/L	NS
375-73-5	Perfluorobutanesulfonic Acid (PFBS)	1.28	2	ng/L	NS
335-76-2	Perfluorodecanoic Acid (PFDA)	0.86	2	ng/L	NS
307-55-1	Perfluorododecanoic Acid (PFDoA)	1.12	2	ng/L	NS
375-85-9	Perfluoroheptanoic Acid (PFHpA)	0.576	2	ng/L	20
355-46-4	Perfluorohexanesulfonic Acid (PFHxS)	1.632	2	ng/L	20
307-24-4	Perfluorohexanoic Acid (PFHxA)	0.564	2	ng/L	NS
375-95-1	Perfluorononanoic Acid (PFNA)	0.604	2	ng/L	20
1763-23-1	Perfluorooctanesulfonic Acid (PFOS)	1.312	2	ng/L	20
335-67-1	Perfluorooctanoic Acid (PFOA)	1.12	2	ng/L	20
376-06-7	Perfluorotetradecanoic Acid (PFTA)	0.632	2	ng/L	NS
72629-94-8	Perfluorotridecanoic Acid (PFTrDA)	0.8	2	ng/L	NS
2058-94-8	Perfluoroundecanoic Acid (PFUnA)	0.968	2	ng/L	NS
	PFAS, Total (5)	0.576	2	ng/L	NS
	PFOA/PFOS, Total	1.12	2	ng/L	NS

NS: No standard for this compound; ng/L: nanograms per liter

Table A.11: Site Metals Contaminants of Concern, Laboratory Quantitation Limits by EPA Methods 6010D, 7471B, 4500-CN-CE, and Action Limits - Soil

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	EPA Industrial Regional Screening Level (RSL)	EPA Residential Regional Screening Level (RSL)	Vermont Residential Screening Levels
7429-90-5	Aluminum, Total	1.08	4	mg/kg	1100000	77000	75600
7440-36-0	Antimony, Total	0.152	2	mg/kg	470	31	27.1
7440-38-2	Arsenic, Total	0.0832	0.4	mg/kg	3	0.68	NS
7440-39-3	Barium, Total	0.0696	0.4	mg/kg	220000	15000	11700
7440-41-7	Beryllium, Total	0.0132	0.2	mg/kg	2300	160	36
7440-43-9	Cadmium, Total	0.0392	0.4	mg/kg	980	71	7.15
7440-70-2	Calcium, Total	1.4	4	mg/kg	NS	NS	NS
7440-47-3	Chromium, Total	0.0384	0.4	mg/kg	NS	NS	NS
7440-48-4	Cobalt, Total	0.0664	0.8	mg/kg	350	23	22.9
7440-50-8	Copper, Total	0.1032	0.4	mg/kg	47000	3100	NS
57-12-5	Cyanide, Total	0.212	1	mg/kg	150	23	NS
7439-89-6	Iron, Total	0.3612	2	mg/kg	820000	55000	53500
7439-92-1	Lead, Total	0.1072	2	mg/kg	800	400	NS
7439-95-4	Magnesium, Total	0.616	4	mg/kg	NS	NS	NS
7439-96-5	Manganese, Total	0.0636	0.4	mg/kg	26000	1800	1170
7439-97-6	Mercury, Total	0.016896	0.08	mg/kg	46	11	10.9
7440-02-0	Nickel, Total	0.0968	1	mg/kg	22000	1500	980
7440-09-7	Potassium, Total	5.76	100	mg/kg	NS	NS	NS
7782-49-2	Selenium, Total	0.1032	0.8	mg/kg	5800	390	382
7440-22-4	Silver, Total	0.1132	0.4	mg/kg	5800	390	247
7440-23-5	Sodium, Total	1.26	80	mg/kg	NS	NS	NS
7440-28-0	Thallium, Total	0.126	0.8	mg/kg	12	0.78	0.764
7440-62-2	Vanadium, Total	0.0812	0.4	mg/kg	5800	390	2.88
7440-66-6	Zinc, Total	0.1172	2	mg/kg	350000	23000	22900

NS: No standard for this compound; mg/kg: milligrams per kilogram

Table A.12: Site Metals Contaminants of Concern, Laboratory Quantitation Limits by EPA Methods 6010D, 7471B, 7470A, 9010C/9012B, and Action Limits - Groundwater

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	VGES
7429-90-5	Aluminum, Total	31.8	100	ug/L	200
7440-36-0	Antimony, Total	0.429	4	ug/L	6
7440-38-2	Arsenic, Total	0.165	0.5	ug/L	10
7440-39-3	Barium, Total	10	10	ug/L	2000
7440-41-7	Beryllium, Total	0.9	5	ug/L	4
7440-43-9	Cadmium, Total	1	5	ug/L	5
7440-70-2	Calcium, Total	35	100	ug/L	NS
7440-47-3	Chromium, Total	2.1	10	ug/L	100
7440-48-4	Cobalt, Total	1.7	20	ug/L	NS
7440-50-8	Copper, Total	2.2	10	ug/L	1300
57-12-5	Cyanide, Total	1.8	5	ug/L	NS
7439-89-6	Iron, Total	9	50	ug/L	300
7439-92-1	Lead, Total	2.7	10	ug/L	15
7439-95-4	Magnesium, Total	15.3	100	ug/L	NS
7439-96-5	Manganese, Total	1.6	10	ug/L	300
7439-97-6	Mercury, Total	0.0915	0.2	ug/L	2
7440-02-0	Nickel, Total	2.4	25	ug/L	100
7440-09-7	Potassium, Total	237	2500	ug/L	NS
7782-49-2	Selenium, Total	3.5	10	ug/L	50
7440-22-4	Silver, Total	10	10	ug/L	100
7440-23-5	Sodium, Total	120	2000	ug/L	250000
7440-28-0	Thallium, Total	0.5	0.143	ug/L	2
7440-62-2	Vanadium, Total	2	10	ug/L	NS
7440-66-6	Zinc, Total	2.1	50	ug/L	5000

NS: No standard for this compound; ug/l: micrograms per liter

Table A.13: Site Herbicide Contaminants of Concern, Laboratory Quantitation Limits by EPA Method 8151A, and Action Limits - Soil

CASNum	Target Analyte	Method Detection Limits	Practical Quantitation Limits	Units	EPA Industrial Regional Screening Level (RSL)	EPA Residential Regional Screening Level (RSL)	Vermont Residential Screening Levels
93-76-5	2,4,5-T	0.0051615	0.1665	mg/kg	8200	630	NS
93-72-1	2,4,5-TP (Silvex)	0.0044289	0.1665	mg/kg	6600	510	NS
94-75-7	2,4-D	0.0104895	0.1665	mg/kg	9600	700	NS
94-82-6	2,4-DB	0.0085581	0.1665	mg/kg	6600	510	NS
75-99-0	Dalapon	0.0108891	0.0333	mg/kg	25000	1900	NS
1918-00-9	Dicamba	0.0055944	0.0333	mg/kg	25000	1900	NS
120-36-5	Dichloroprop	0.0095571	0.0333	mg/kg	NS	NS	NS
94-74-6	MCPA	0.94239	3.33	mg/kg	410	32	NS
93-65-2	MCPP	1.04895	3.33	mg/kg	820	63	NS

NS: No standard for this compound; mg/kg: milligrams per kilogram

Appendix B: Detailed Cost Estimate

Long Falls Paperboard Phase II ESA
19-015
DETAILED FEE & SCOPE DETAILS

#	Staff Type	Name	Rate Per Unit	Unit	Amount	Subtotal	Scope Details
1	**Task 1 - Project Coordination, SSQAPP, HASP, Digsafe, Development of Existing Wells**						Prepare Work Plan in accordance with the I-Rule. Prepare a site specific Health and Safety Plan.
	Professional Services						
	Senior Professional 2	DAA	$ 115 / hour	12	$1,380		Includes obtaining and review of WSWMD files related to groundwater at the Site.
	Project Professional 2	LJR	$ 100 / hour	20	$2,000		
	Staff Professional 2	WR	$ 80 / hour	8	$640		
	Senior Professional 3	KBW	$ 115 / hour	1	$115		Includes overall project management (DAA): coordination with team, and updates to stakeholders. Includes invoicing time.
	Staff Professional 3	BMD	$ 80 / hour	10	$800		
		Professional Services Summary		*51*		*$4,935*	Stone will perform an initial site visit and dig safe mark-out.
	Consultants*						
	Private Utility Locator		$1,040 ea	1	$1,144		Staff:
		Consultant Summary				*$1,144*	Senior Professional:
	Stone Equipment						- Overall Project Coordination (8)
	Tacoma Mileage		$0.58 / mile	452	$262.16		- Work Plan/HASP Review (4)
	GDS Trimble GEO 7X GPS		$125 / day	1	$125.00		Project Professional:
	EAR Interface Probe		$55 / day	1	$55.00		- Draft Work Plan/HASP (16)
		Expense Summary				*$442*	- Review WSWMD information (4)
							Staff Professional:
							- Draft Work Plan Figures (8)
							- Utility location oversight/contingent well development (10)
	TASK SUBTOTAL					**$6,521**	A Stone subcontractor with Stone oversight will attempt to locate private utilities at the Site.
2	**Task 2 - Soil Assessment**						Includes up to 5 days of field work, 3 with Geoprobe.
	Professional Services						
	Project Professional 2	LJR	$ 100 / hour	50	$5,000		Mob/demob (travel)
	Staff Professional 1	DTC	$ 70 / hour	50	$3,500		- Project and staff professional (4 hrs each)
		Professional Services Summary		*100*		*$8,500*	Dye Test Maintenance Area Floor Drain
							- Project and staff professional (2 hrs ea)
	Consultants*						
	EAI - Mob/Demob		$275 / ls	1	$303		Surface soil sampling RECs 5, 6, 9
	EAI - Geoprobe, Support Vehicle, & Labor		$1,450 / day	3	$4,785		- Project and staff professional (6 hrs ea)
	EAI - Consumables		$400 / day	3	$1,320		
	EAI - Per Diem		$325 / day	3	$1,073		DU1 & DU2 Sampling
	Alpha - Soil VOCs		$71 / sample	23	$1,796		- Project and staff professional (8 hrs ea)
	Alpha - Soil SVOCs		$120 / sample	21	$2,772		
	Alpha - Soil Dioxins/Furans		$500 / sample	8	$4,400		Subsurface soil sampling up to 25 fbgs
	Alpha - Soil PCB Aroclors		$45 / sample	11	$545		- Project and staff professional (10 hrs ea)
	Alpha - Soil PFAS		$275 / sample	9	$2,723		
	Alpha - Soil TAL Metals + Cn		$120 / sample	16	$2,112		Deep subsurface soil profile and sampling to approx 80 fbgs
	Alpha - Soil PAHs		$70 / sample	7	$539		- Project and staff professional (20 hrs ea)
	Alpha - Soil Herbicides		$135 / sample	7	$1,040		
		Consultant Summary				*$23,406*	
	External Expenses						
	Field Supplies & Equipment		$25 / day	5	$138		
	Per Diem/Meals (non lodging)		$55 / day	10	$605		
	Shipping/Freight		$75 / ea	5	$413		
	Lodging		$94 / ea	10	$1,034		
	Stone Equipment						
	Tacoma Mileage		$0.58 / mile	300	$174		
	EAR PID		$90 / day	5	$450		
	GDS Trimble GEO 7X GPS		$125 / day	1	$125		
	Stone Consumables						
	EAR PPE		$15 / day/staff	5	$75		
		Expense Summary				*$3,013*	
	TASK SUBTOTAL					**$34,919**	
3	**Task 3 - Groundwater Assessment**						Includes approximately 3 days of field work.
	Professional Services						
	Project Professional 2	LJR	$ 100 / hour	40	$4,000		Mob/demob (travel)
	Staff Professional 1	DTC	$ 70 / hour	40	$2,800		- Project and staff professional (4 hrs each)
		Professional Services Summary		*80*		*$6,800*	Groundwater sampling at approximately 80 fbgs
							- Project and staff professional (36 hrs ea)
	Consultants*						
	EAI - Geoprobe, Support Vehicle, & Labor		$1,450 / day	3	$4,785		Cost estimate does not include sampling groundwater monitoring wells that existed in 1994, if located.
	EAI - Per Diem		$325 / day	3	$1,073		
	EAI - Per Diem		$325 / day	3	$1,073		
	Alpha - GW VOCs		$60 / sample	15	$990		
	Alpha - GW SVOCs		$120 / sample	11	$1,452		
	Alpha - GW Dioxins/Furans		$500 / sample	3	$1,650		
	Alpha - GW PCB Aroclors		$45 / sample	3	$149		
	Alpha - GW PFAS		$250 / sample	15	$4,125		
	Alpha - GW TAL Metals + Cn		$120 / sample	12	$1,584		
		Consultant Summary				*$16,880*	
	External Expenses						
	Field Supplies & Equipment		$25 / day	3	$83		
	Per Diem/Meals (non lodging)		$55 / day	6	$363		

Long Falls Paperboard Phase II ESA
19-015
DETAILED FEE & SCOPE DETAILS

#	Staff Type	Name	Rate Per Unit	Unit	Amount	Subtotal		Scope Details
	Shipping/Freight		$75 / ea	3	$248			
	Lodging		$94 / ea	6	$620			
	Rental-Field Equipment		$135 ea	3	$446			
	Watera Pump		$92 day	3	$304			
	Stone Equipment							
	Tacoma Mileage		$0.58 / mile	300	$174.00			
	EAR Electrical Generator - Honda Eu 2000		$50.00 / day	3	$150.00			
	Stone Consumables							
	EAR 55-Gallon Drum		$71.50 / ea	2	$143			
	EAR PPE		$15 / day/staff	6	$90			
	EAR 1/4" OD FEP Tubing SG		$2.16 / foot	1000	$2,160			
			Expense Summary			*$4,780*		
	TASK SUBTOTAL						**$28,459**	
4	**Task 4 - Data Evaluation & Reporting**							Includes:
	Professional Services							
	Senior Professional 2	DAA	$ 115 / hour	16	$1,840			Daily briefs to VT DEC during field activities - assumes 8 days, 1 hr per day for Senior professional.
	Project Professional 2	LJR	$ 100 / hour	32	$3,200			
	Staff Professional 2	WR	$ 80 / hour	16	$1,280			
			Professional Services Summary	*64*		*$6,320*		
	Consultants*							
			$0		$0			
			$0		$0			
			$0		$0			
			Consultant Summary			*$0*		
	External Expenses							
			$0.000 /		$0			
	Stone Equipment							
			$0.00 /		$0.00			
	Stone Consumables							
			$0.00 /		$0.00			
			Expense Summary			*$0*		
	TASK SUBTOTAL						**$6,320**	
	PROJECT TOTAL						***$76,219***	

**Stone Environmental's standard mark-up on all Consultant and reimbursable project expenses is 10%.*

Appendix C: Stone and Laboratory Standard Operating Procedure

STANDARD OPERATING PROCEDURE

SEI-5.94.0

Procedure for the Collection of Groundwater to be Analyzed for Per-and Polyfluoroalkyl Substances (PFAS)

SOP Number: SEI-5.94.0
Revision Number: NA
Date Issued: 08/27/2018
Date of Revision: NA

1.0 OBJECTIVE

The purpose of this Standard Operating Procedure (SOP) is to detail the sampling methods used to collect groundwater to be analyzed for Per- and Polyfluoroalkyl Substances (PFAS). Stone Environmental, Inc. (Stone) utilizes a wide variety of techniques for the collection of groundwater samples as detailed in SEI SOP 6.27.*n Groundwater Sampling of Monitoring Wells* and SEI SOP 6.34.*n Procedure for Sampling Groundwater Monitoring* Wells Using Low Stress (Low Flow) Technique. The SOP will not detail one specific groundwater sampling technique but will discuss methods that can be used across all sampling techniques.

2.0 POLICIES

It is the policy of Stone that all field staff conducting PFAS sampling read this SOP prior to collecting samples.

Stone personnel will legibly record data and observations in the field to enable others to reconstruct project events and provide sufficient evidence of activities conducted. Field personnel will use a field logbook, observation and remark (O&R) form, or other designated form to record activities, measurements, and observations made in the field.

3.0 SAFETY ISSUES

The corporate Health and Safety Plan (HASP) and the Site-Specific Health and Safety Plan specify the procedures to be followed and equipment to be used during site activities. The following is a brief and general overview of safety issues:

- Those associated with the operation of drill rigs;
- Overhead and underground utility hazards;
- Traffic/motor vehicle hazards;
- Exposure to contaminants potentially present in site groundwater;
- Slip, trip, and fall hazards;
- Poisonous plants and dangerous animals;

- Pinch Points;
- Compressed gas hazards;
- Fire hazards from hot work (e.g., grinding);
- Gasoline hazards (filling generator)

Stone staff will read and understand the Site-Specific Health and Safety Plan, prior to conducting groundwater sampling for the analysis of PFAS.

Stone staff and others under contract with Stone will wear appropriate personal protective clothing as outlined in the site-specific health and safety plan. This may include, but not be limited to:

- A hardhat when overhead hazards are present;
- Eye protection;
- Hearing protection;
- Steel toed boots (always to be worn on all sites);
- Appropriate clothing for weather conditions (e.g., rain gear for wet conditions, sunscreen for UV protection, and layered clothing during cold sampling events.) subject to the requirements for the method (e.g., no Gore-tex™, etc.)

4.0 PROCEDURES

4.1 Introduction

The United States Environmental Protection Agencies (EPAs) health advisory level for PFAS in drinking water is currently set at 70 parts per trillion (ppt) and the Vermont drinking water level for PFAS is 20 ppt. Due to these low regulatory levels, it is important for the proper equipment and clothing to be used and worn while collecting groundwater samples to be analyzed for PFAS because PFAS can be present in sampling equipment and bottleware as well as clothing and personal care products that are typically used and/or worn while collecting groundwater samples. These items can include but are not limited to the following: Teflon lined tubing, low density polyethylene (LDPE) or glass bottles, waterproof field books, sharpies, synthetic or waterproof clothing including Gore-Tex and coated nylons, cosmetics, and pre-packaged foods. Detection of PFAS at low levels can be affected by the presence of the aforementioned materials being present on-site while sampling.

Stone utilizes varying techniques to collect groundwater samples as detailed in SEI SOP 6.27.*n Groundwater Sampling of Monitoring Wells* and SEI SOP 6.34.*n Procedure for Sampling Groundwater Monitoring* Wells Using Low Stress (Low Flow) Technique. The general techniques discussed in SEI SOP 6.27.*n* and SEI SOP 6.34.*n* will be utilized for the collection of groundwater, however, when collecting samples for PFAS analysis this SOP will supersede aspects of those SOPs (e.g., equipment and sample collection) to prevent potential cross-contamination of PFAS from background sources.

4.2 Equipment

- Extraction Device: Submersible pumps (Centrifugal or bladder pumps), peristaltic pumps, or bailers. **Extraction devices must not be Teflon lined or made of fluoropolymer containing materials**. Dedicated and/or disposable stainless steel or high-density polyethylene (HDPE) equipment must be used for sampling instead.
- Tubing (if applicable): HDPE, silicon, polyvinyl chloride (PVC), and stainless-steel tubing are acceptable materials to be used for tubing. **Tubing must not be Teflon lined, low density polyethylene, or made of fluoropolymer containing materials (e.g., FEP, PTFE, etc.)**. When tubing is used for sampling it must be dedicated solely for use for PFAS sampling.
- Power Source (if applicable): Generator, battery, nitrogen tank.
- Decontamination Supplies: Alconox or Liquinox, laboratory supplied PFAS-free water, and a plastic brush.
- Sample Bottles: Contract laboratory supplied bottles specifically for PFAS sampling: HDPE or polypropylene bottles with an unlined (**no Teflon or fluoropolymer lined caps**), polypropylene, or HDPE screw cap. **Glass and LDPE containers shall not be used. Laboratory provided labels that have been tested to confirm they are "PFC-Free" may be used, all other non-tested samples labels shall not be used.**
- Sample Preservation: Ice. **Chemical ice packs must not be used.**
- Record Keeping Supplies: Paper, aluminum clip board, Sharpies, ball point pen are allowed. **Non-Sharpie markers, waterproof paper or field books, plastic clipboards, and adhesive paper products must not be used. Laboratory supplied sample labels that have been tested and confirmed to not contain PFCs may be used, all other non-tested samples labels shall not be used.**
- Nitrile Gloves

4.3 Personal Equipment

The following requirements must be met prior to arriving on-site to prevent potential cross contamination while sampling for PFAS.

- Personal hygiene products (e.g., cosmetics, lotions, and moisturizes) must not be worn.
- Clothing must be well washed (brand new clothing shall not be worn during sampling) and made of synthetic or natural fibers. **Waterproof, water resistant, stain resistant, and clothing washed in fabric softeners must not be worn during sampling.**
- Boots must be made with polyurethane or PVC. **Waterproof, water resistant, and stain resistant boots must not be worn during sampling.**
- Sunscreen and insect repellants must not be used unless they are on the approved list:
    - Sunscreen: Alba Organics Natural, Yes to Cucumbers, Aubrey Organics, Jason Natural Sun Block, Kiss my Face, Baby-safe sunscreens (free or natural)

- Insect Repellents: Jason Natural Quit Bugging Me, Repel Lemon Eucalyptus, Herbal Armor, California Baby Natural Bug Spray, BabyGanics

- **Prepackaged food, Tupperware containers, and fast food wrappers must not be brought close to the sampling location**.

4.4 Procedure

Further detail discussing groundwater sampling techniques are provided in SEI SOP 6.27.*n Groundwater Sampling of Monitoring Wells* and SEI SOP 6.34.*n Procedure for Sampling Groundwater Monitoring Wells Using Low Stress Technique*. The following procedure are specific steps that must be taken during groundwater sampling to prevent potential cross-contamination.

4.4.1 Initial Setup

1. Prior to sampling, all non-dedicated sampling equipment (equipment that has been previously used) shall be decontaminated. Decontamination procedures are detailed in section 4.5
2. Staff collecting samples shall wash their hands prior to completing sampling and shall wear nitrile gloves.
3. PFAS sample bottles shall be stored separately from sample bottles that are used for other parameters (these may contain PFAS).
4. Remove any potential PFAS containing materials away from the sampling location (e.g., dedicated tubing in monitoring wells that may be Teflon lined).
5. Check to ensure sampling equipment, bottles, and other materials located within the sampling area are in accordance with the requirements discussed in Sections 4.1, 4.2, and 4.3.
6. Install the required extraction device and complete purging in accordance with sampling techniques described in SEI SOP 6.27.*n Groundwater Sampling of Monitoring Wells* and SEI SOP 6.34.*n Procedure for Sampling Groundwater Monitoring Wells Using Low Stress Technique*.

4.4.2 Sample Collection

Groundwater samples collected for PFAS analysis will be collected in accordance to the procedures detailed in SEI SOP 6.27.*n Groundwater Sampling of Monitoring Wells* and SEI SOP 6.34.*n Procedure for Sampling Groundwater Monitoring Wells Using Low Stress Technique*, with the following exceptions:

1. PFAS samples will be collected first if additional samples for other parameters are being collected from the same location.
2. The sample bottle cap must not be placed on the ground or come in contact with any other surface while collecting the sample. In addition, contact with the inside of the bottle and cap must be avoided.

3. **PFAS samples must never be filtered.**
4. Once the sample is collected and capped, it shall be placed in an individually sealed plastic bag separate from all other sample parameter bottles (non-PCF bottles) in a cooler filled with ice. The ice shall be bagged to prevent melt water from contacting the sample bottle.
5. Samples will be shipped to the laboratory in accordance with SEI SOP 6.16.*n Handling, Collection, and Transportation of Samples* for analysis of PFAS by the laboratory's SOP for EPA Method 537.

4.5 Decontamination

Decontamination procedures are further discussed in SEI SOP 5.1.*n Maintenance and Decontamination of Field Equipment* and SEI SOP 6.34.*n Procedure for Sampling Groundwater Monitoring Wells Using Low Stress Technique,* however, the following techniques shall be implemented when PFAS sampling is being completed.

- Alconox or Liquinox are the only two soaps that shall be used to decontaminate non-dedicated PFAS sampling equipment.
- Water used for decontamination shall be laboratory certified as "PFAS-free".

Equipment will first be rinsed with laboratory-supplied "PFAS-free" water, then scrubbed with an Alconox or Liquinox solution using a plastic brush, then rinsed again using the "PFAS-free" water.

4.6 Quality Assurance/Quality Control

Quality Control (QC) samples (e.g., trip, field, and equipment blanks, as well as field duplicates) will be collected in accordance to the site Quality Assurance Project Plan, if applicable, or as specified in the site work plan. However, due to the increased risk of cross-contamination a field and equipment blank shall be collected during a PFAS sampling event.

QC samples are required to verify that the sample collection and handling process has not compromised the quality of the groundwater samples. All field QC samples must be prepared the same as regular investigation samples with regards to sample volume, containers, and preservations.

If relative contaminant concentrations are known, collect samples in order from wells with the lowest contaminant concentration to the highest. Collect equipment blanks after sampling contaminated wells and not after background wells.

4.6.1 Equipment Blanks

If non-dedicated equipment is being used during PFAS sampling, rinsate using "PFAS-free" water will be collected from the sampling equipment following the equipment decontamination.

If dedicated equipment is being used (e.g., tubing), then water will be poured or pumped through the equipment to confirm the absence of PFAS within the equipment.

4.6.2 Field Blanks

Field blanks will be collected using laboratory provided bottles and "PFAS-free" water. Field blanks will be collected prior to collecting PFAS samples from a designated location. Sampling will be completed by pouring "PFAS-free" water from a sealed laboratory provided bottle into an empty laboratory supplied bottle.

4.7 Documentation

A record of the sample collection must be made in the field at the time the sample is collected. The record should be made in a field notebook, a sample collection form, or other medium acceptable according to the work plan. The information to be recorded must, at a minimum, include the following:

- Date and time of sample collection;
- Name(s) of the personnel performing the sampling;
- Weather;
- Sample location, well identification, and / or sample identification;
- Project/study designation;
- Type of pump used;
- Description of all sampling/monitoring equipment used, including trade names, model number, instrument identification number, diameters, material composition, etc.
- Types of sample bottles and preservatives used;
- Parameters requested for analysis; and
- Field observations during sampling event, including problems encountered;

5.0 RESPONSIBILITIES

Stone staff are required to take accurate and descriptive notes. Variations from the SOP should be noted on observations and remarks (O&R) forms along with data and personnel.

Field staff members are responsible for following and implementing all procedures outlined within this SOP. Care shall be taken to avoid compromising sample and data integrity.

6.0 DEFINITIONS

1. *EPA:* the U.S. Environmental Protection Agency.
2. *Dedicated Equipment:* Equipment that is used only once at a designated sampling location. Dedicated equipment does not need to be decontaminated prior to or following sampling. Dedicated sampling equipment is disposed of immediately following its use.
3. *FEP:* Fluorothyelene propylen*e.*
4. *HDPE: High-density polyethylene*
5. *Non-Dedicated Equipment:* Equipment that is used more than once during a sampling event. Once non-dedicated sampling equipment is used, it must be decontaminated prior to collecting additional samples.

6. *Observations & Remarks Form (O&R):* A pre-printed form, which contains mostly blank space for general note taking. The form typically prompts the user for the study or project designation, the SEI project number, the client or sponsor name, the total number of pages (page *n* of n) and requires a signature and date. The form is generally used to capture notes of one person when another, more specific forms is not available.
7. *PFAS:* Per- and Polyfluoroalkyl Substances.
8. *ppt:* Parts per trillion.
9. *PFC*: Per-Fluorinated Compounds
10. *PTFE*: Polytetrafluoroethylene.
11. *PVC*: Polyvinyl chloride

7.0 REFERENCES

NHDES, Per-Fluorinated Compound (PFC) Sample Collection Guidance
(https://www.des.nh.gov/organization/commissioner/documents/pfas-sample-guidance-201611.pdf)

8.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

None

9.0 AUTHORIZATION

Written by: _____ Date: 08/27/18

Brian Diezel, Engineer

Approved by: _____ Date: 8/27/2018

John Hanzas, President

10.0 REVISION HISTORY

N/A

Dioxins and Furans by High-Resolution GC/MS

References: **EPA 8290A,** Polychlorinated Dibenzopdioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/HighResolution Mass Spectrometry (HRGC/HRMS), SW-846 Test Methods for Evaluating Solid Waste, Update IV, 2/2007.

EPA 8000D, SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Revision IV, March 2014.

EPA 3500C, SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, 2007.

Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.2, 2018.

1. Scope and Application

Matrices: Aqueous, Soil, and Tissue matrices.

Definitions: Refer to Alpha Analytical Quality Manual.

1.1 This is a High resolution Mass Spectrometer method for the detection and quantitative measurement of polychlorinated dibenzo-*p*-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) in a variety of environmental matrices and at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations. Accuracy and precision data have been generated for the compounds listed in Table 1.

1.2 The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the operation of the HRMS and in the interpretation of HRMS data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

Table 1	
Parameter	**CAS**
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin (PeCDD)	40321-76-4
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	39227-28-6
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	57653-85-7
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin (HxCDD)	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin (HpCDD)	35822-46-9
Octachlorodibenzo-*p*-dioxin (OCDD)	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	51207-31-9
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	57117-41-6
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	57117-31-4
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	70648-26-9
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	72918-21-9
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	60851-34-5
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	55673-89-7
Octachlorodibenzofuran (OCDF)	39001-02-0
Total Tetrachlorodibenzo-*p*-dioxin (TCDD)	41903-57-5
Total Pentachlorodibenzo-*p*-dioxin (PeCDD)	36088-22-9
Total Hexachlorodibenzo-*p*-dioxin (HxCDD)	34465-46-8
Total Heptachlorodibenzo-*p*-dioxin (HpCDD)	37871-00-4
Total Tetrachlorodibenzofuran (TCDF)	55722-27-5
Total Pentachlorodibenzofuran (PeCDF)	30402-15-4
Total Hexachlorodibenzofuran (HxCDF)	55684-94-1
Total Heptachlorodibenzofuran (HpCDF)	38998-75-3

2. Summary of Method

This procedure uses matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary column gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) analytical techniques. See Method 3500 for guidance on other appropriate extraction techniques.

A designated amount (see Table 1) of soil, sediment, fly ash, water, and sludge (including paper pulp) is spiked with a solution containing specified amounts of each of the fifteen isotopically (13C12) labeled PCDDs/PCDFs listed in the far left column of Table 2. The sample is then extracted according to a matrix-specific extraction procedure. Aqueous samples that contain 1 percent or more solids and solid samples that show an aqueous phase are filtered, the solid phase (including the filter) and the aqueous phase extracted separately, and the extracts combined before extract cleanup. The extraction procedures are:

Toluene -- Soxhlet extraction for soil, sediment, fly ash, and paper pulp samples

- Toluene -- Microwave extraction for soil, sediment, fly ash, Tissue and paper pulp samples
- Toluene -- Solid Phase Extraction of water samples.

Table 2		
Parameter	**Sample Fortification Solution Concentration (pg/µl)**	**Recovery Standard Solution Concentration (pg/µl)**
$^{13}C_{12}$-2,3,7,8-TCDD	100	--
$^{13}C_{12}$-2,3,7,8-TCDF	100	--
$^{13}C_{12}$-1,2,3,4-TCDD	--	200
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	--
$^{13}C_{12}$--1,2,3,7,8-PeCDF	100	--
$^{13}C_{12}$--2,3,4,7,8-PeCDF	100	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	--	200
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	--
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	--
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	--
$^{13}C_{12}$-OCDD	200	--

The extracts are treated with silica gel impregnated with sulfuric acid before chromatography on activated carbon.

The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding 5 µL of a nonane solution containing 200 pg/µL of the recovery standards 13C12-1,2,3,4-TCDD and 13C12-1,2,3,7,8,9-HxCDD (Table 2). The former is used to determine the percent recoveries of tetra- and pentachlorinated PCDD/PCDF congeners, while the latter is used to determine the percent recoveries of the hexa-, hepta- and octachlorinated PCDD/PCDF congeners.

An aliquot of the concentrated extract is injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving power of at least 10,000 (10 percent valley definition).

The identification of OCDD and fifteen 2,3,7,8-substituted congeners (Table 3), for which 13C-labeled standards are available in the sample fortification and recovery standard solutions (Table 2), is based on their elution at their exact retention time (within 0.005 retention time units measured in the routine calibration) and the simultaneous quantitation of the two most abundant ions in the molecular ion region. The remaining two 2,3,7,8-substituted congeners for which may exhibit a chromatographic interference (OCDF) or which are used as an internal standard (1,2,3,7,8,9-HxCDD), and all other PCDD/PCDF congeners are identified when their relative retention times fall within their respective PCDD/PCDF retention time windows, as established from the routine calibration data, and the simultaneous quantitation of the two most abundant ions in the molecular ion region. The identification of OCDF is based on its retention time relative to 13C12-OCDD and the simultaneous quantitation of the two most abundant ions in the molecular ion region. Identification also is based on a comparison of the ratios of the integrated ion abundance of the molecular ion species to their theoretical abundance ratios.

Table 3		
Parameter	**Internal Standard used Quantitation**	**Recovery Standard used for Labeled Recovery**
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TeCDD
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	$^{13}C_{12}$-1,2,4,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TeCDD
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-,2,3,7,8,9-HxCDD
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-,2,3,7,8,9-HxCDD
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)	$^{13}C_{12}$--1,2,3,6,7,8-HxCDD	--
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)	$^{13}C_{12}$—1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-,2,3,7,8,9-HxCDD
Octachlorodibenzo-p-dioxin (OCDD)	$^{13}C_{12}$-OCDD	$^{13}C_{12}$-,2,3,7,8,9-HxCDD
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TeCDD
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	$^{13}C_{12}$-1,2,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TeCDD
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TeCDD
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-,2,3,7,8,9-HxCDD
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-,2,3,7,8,9-HxCDD
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-,2,3,7,8,9-HxCDD
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-,2,3,7,8,9-HxCDD
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-,2,3,7,8,9-HxCDD
Octachlorodibenzofuran (OCDF)	$^{13}C_{12}$-OCDD	--
Total Tetrachlorodibenzo-*p*-dioxin (TCDD)	$^{13}C_{12}$-2,3,7,8-TCDD	--
Total Pentachlorodibenzo-*p*-dioxin (PeCDD)	$^{13}C_{12}$-1,2,4,7,8-PeCDD	--
Total Hexachlorodibenzo-*p*-dioxin (HxCDD)	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	--
Total Heptachlorodibenzo-*p*-dioxin (HpCDD)	$^{13}C_{12}$—1,2,3,4,6,7,8-HpCDD	--
Total Tetrachlorodibenzofuran (TCDF)	$^{13}C_{12}$-2,3,7,8-TCDF	--
Total Pentachlorodibenzofuran (PeCDF)	$^{13}C_{12}$-1,2,4,7,8-PeCDF	--
Total Hexachlorodibenzofuran (HxCDF)	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	--
Total Heptachlorodibenzofuran (HpCDF)	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	--

Quantitation of the individual congeners, total PCDDs, and total PCDFs is achieved in conjunction with the establishment of a multipoint (five points) calibration curve for each homologue, during which each calibration solution is analyzed once.

2.1 Method Modifications from Reference

None.

3. Reporting Limits

The reporting limit for PCDD and PCDF congeners based on level of chlorination are listed in Table 4.

Table 4		
Parameter	**Soil, Sediment, Solid Matrices (pg/g)**	**Aqueous Matrices (pg/L)**
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	.5	10
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	2.5	50
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	2.5	50
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	2.5	50
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)	2.5	50
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)	2.5	50
Octachlorodibenzo-p-dioxin (OCDD)	5	100
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	.5	10
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	2.5	50
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	2.5	50
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	2.5	50
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	2.5	50
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	2.5	50
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	2.5	50
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	2.5	50
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	2.5	50
Octachlorodibenzofuran (OCDF)	5	100
Total Tetrachlorodibenzo-*p*-dioxin (TCDD)	.5	10
Total Pentachlorodibenzo-*p*-dioxin (PeCDD)	2.5	50
Total Hexachlorodibenzo-*p*-dioxin (HxCDD)	2.5	50
Total Heptachlorodibenzo-*p*-dioxin (HpCDD)	2.5	50
Total Tetrachlorodibenzofuran (TCDF)	.5	10
Total Pentachlorodibenzofuran (PeCDF)	2.5	50
Total Hexachlorodibenzofuran (HxCDF)	2.5	50
Total Heptachlorodibenzofuran (HpCDF)	2.5	50

4. Interferences

4.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. In addition, analysts should avoid using PVC gloves. Also refer to Method 8000 for a discussion of interferences.

4.2 The use of high-purity reagents and pesticide-grade solvents helps to minimize interference problems. Purification of solvents by distillation, in all glass systems, may be required.

4.3 Interferants coextracted from the sample will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans, that may be found at

concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the established retention time windows. While cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve the sensitivity described in this method.

4.4 A high-resolution capillary column is used in this method. However, no single column is known to resolve all 210 isomers. The 60-m RTX-Dioxin2 GC column is capable of 2,3,7,8-TCDD and 2,3,7,8-TCDF isomer specificity (Sec. 6.2.1 of EPA 8290A). A verification of this specificity is analyzed daily. Where applicable, a high-resolution capillary column (60-m DB-5, J&W Scientific, or equivalent) is to be used. However, the 60-m DB-5 GC column is only capable of 2,3,7,8-TCDD isomer specificity (Sec. 6.2.1 of EPA 8290A). In order to determine the concentration of the 2,3,7,8-TCDF (if detected on the DB-5 column), the sample extract must be reanalyzed on a column capable of 2,3,7,8-TCDF isomer specificity (RTX-Dioxin2 or equivalent).

5. Health and Safety

5.1 The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

5.2 All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.3 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed.

5.4 The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The analyst should note that finely divided dry soils contaminated with PCDDs and PCDFs are particularly hazardous because of the potential for inhalation and ingestion. It is recommended that such samples be processed in a confined environment, such as a hood or a glove box. Laboratory personnel handling these types of samples should wear masks fitted with charcoal filters to prevent inhalation of dust.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Collect samples in amber glass containers following conventional sampling practices. Aqueous samples that flow freely are collected in refrigerated bottles using automatic sampling equipment. Solid samples are collected as grab samples using wide-mouth jars.

6.2 Sample Preservation

6.2.1 Maintain aqueous samples in the dark at 0-4°C from the time of collection until receipt at the laboratory. If residual chlorine is present in aqueous samples, add 80

mg sodium thiosulfate per liter of water. If sample pH is greater than 9, adjust to pH 7-9 with sulfuric acid.

6.2.2 Maintain solid, semi-solid, oily, and mixed-phase samples in the dark at <4°C from the time of collection until receipt at the laboratory.

6.2.3 Store aqueous samples in the dark at 0-4°C. Store solid, semi-solid, oily, mixed-phase, and tissue samples in the dark at <-10°C.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

6.4.1 There are no demonstrated maximum holding times associated with CDDs/CDFs in aqueous, solid, semi-solid, tissues, or other sample matrices. If stored in the dark at 0-4°C and preserved as given above (if required), aqueous samples may be stored for up to one year. Similarly, if stored in the dark at <-10°C, solid, semi-solid, multi-phase, and tissue samples may be stored for up to one year.

6.4.2 Store sample extracts in the dark at <-10°C until analyzed. If stored in the dark at <-10°C, sample extracts may be stored for up to one year.

7. Equipment and Supplies

7.1 High-resolution gas chromatograph / high-resolution mass spectrometer / data system (HRGC/HRMS/DS)

The GC must be equipped for temperature programming, and all required accessories must be available, such as syringes, gases, and capillary columns.

7.1.1 GC injection port -- The GC injection port must be designed for capillary columns using split-less injections of 1-µL. When using the method described in this protocol, a 1-µL injection volume is used consistently (i.e., the injection volumes for all extracts, blanks, calibration solutions and the performance check samples are 1 µL.

7.1.2 GC/MS interface -- The GC/MS interface components should withstand 350 EC. The interface must be designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. Cold spots or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening.

7.1.3 Mass spectrometer -- The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley).

7.1.4 Data system -- A dedicated data system is employed to control the rapid multiple-ion monitoring process and to acquire the data. Quantitation data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantitations may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The data system must be capable of acquiring data at a minimum of 10 ions in a single scan. It is also recommended to have a data system capable of switching to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system should be able to provide hard copies of individual ion chromatograms for selected gas chromatographic time intervals. It should also be able to acquire mass spectral

peak profiles and provide hard copies of peak profiles to demonstrate the required resolving.

7.2 GC columns: Fused-silica capillary columns capable of demonstrating the required separation of all 2,3,7,8-specific isomers whether a dual-column or a single-column analysis is chosen. Chromatographic performance must be demonstrated and documented at the beginning of each 12-hr period (after mass resolution and GC resolution are demonstrated) during which sample extracts or concentration calibration solutions will be analyzed.

7.3 Microwave Extraction Unit.

7.3.1 Capable of sensing the temperature to within ± 2.5 EC and automatically adjusting the microwave field output power within 2 sec of sensing. Temperature sensors should be accurate to ± 2 EC. Temperature feedback control provides the primary performance mechanism for this method.

7.3.2 Microwave extraction vessels that can accommodate 1-g to 20-g samples. Vessels should be transparent to microwave energy, relatively inert to reagents and sample components, and capable of withstanding the temperature and pressure specifications (minimum conditions of 200 EC and 200 psi) necessary to perform this procedure. Follow the manufacturer's instructions regarding cleaning, handling, and sealing the vessels.

7.4 Solid Phase Extraction Manifold.

Manifold capable of holding multiple disks or cartridges fitted with a vacuum pump.

7.5 Nitrogen Assisted Water Bath.

7.5.1 Capable of regulating temperature to +/- 1 degree C.

7.5.2 Capable of applying a gentle stream of nitrogen +/- 1 PSI.

7.6 Soxhlet

7.7 All glass Soxhlet apparatus with 500-mL flask.

7.8 Auto Pipettes in 10, 100, 1000 µl increments.

7.9 Low volume GC auto-sampler vials.

7.10 4 ml amber screw cap vials

7.11 12 ml amber screw cap vials.

7.12 Glass Pasteur pipettes

7.13 Metal Spatulas

7.14 Glass wool: Purified by heating to 400°C for 1 hour.

7.15 Teflon powder funnels

7.16 Filter paper: Number 40, 150mm ashless circles

7.17 pH Paper: Multibanded, wide range

8. Reagents and Standards

8.1 Organic-free reagent water -- All references to water in this method refer to organic-free reagent water.

8.2 Sulfuric acid, H_2SO_4, concentrated, ACS grade, specific gravity 1.84.

8.3 Solvents -- All solvents should be (at a minimum) pesticide quality or equivalent, distilled-in-glass.

8.3.2 Hexane, C_6H_{14}.

8.3.3 Nonane, C_9H_{20}.

8.3.4 Dodecane, $C_{12}H_{26}$.

8.3.5 Toluene, $C_6H_5CH_3$.

8.3.6 Acetone, CH_3C0CH_3.

8.3.7 Methanol, CH_3OH.

8.4 High-resolution concentration calibration (HRCC) solutions (Table 5) -- Five nonane solutions containing 17 unlabeled and 17 carbon-labeled PCDDs and PCDFs at known concentrations are used to calibrate the instrument. The concentration ranges are homologue-dependent, with the lowest values for the tetrachlorinated dioxin and furan (.5 pg/µL) and the highest values for the octachlorinated congeners (2000 pg/µL). A complete list of calibration standards is listed in Table 4. All standards should be stored away from any light not in use, and should be freshly prepared once a year, or sooner if check standards indicate a problem. The calibration verification (GC column performance check) standard should be prepared, as necessary. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

8.5 GC column performance check (evaluation) solution -- This solution contains the first and last eluting isomers for each homologous series from tetra- through heptachlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. The solution also contains the analyte mixture of the calibration CS L3 standard solution prepared from an independent lot. Table 5 summarizes the qualitative composition of this performance evaluation solution.

8.6 Sample fortification solution -- This nonane solution contains the 15 internal standards at the nominal concentrations that are listed in Table 2. The solution contains at least one carbon-labeled standard for each homologous series, and it is used to measure the concentrations of the native substances.

8.7 Recovery standard solution -- This nonane solution contains two recovery standards, 13C12-1,2,3,4-TCDD and 13C12-1,2,3,7,8,9-HxCDD, at a nominal concentration of 200 pg/µL per compound. 5 µL of this solution will be spiked into each sample extract before the final concentration step and HRGC/HRMS analysis.

8.8 Clean-up Standard Solution. This is a nonane solution containing $^{37}Cl_4$-2,3,7,8-TCDD at 8 ng/ml. 12.5 µl of this solution is spiked into each sample extract prior to the clean-up procedure

Table 5

Target Analyte	CS L1 pg/µl	CS L2 pg/µl	CS L3 pg/µl	CS L4 pg/µl	CS L5 pg/µl

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	.5	2	10	40	200
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	2.5	10	50	200	1000
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	2.5	10	50	200	1000
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	2.5	10	50	200	1000
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)	2.5	10	50	200	1000
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)	2.5	10	50	200	1000
Octachlorodibenzo-p-dioxin (OCDD)	.5	20	100	400	2000
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	.5	2	10	40	1000
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	2.5	10	50	200	1000
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	2.5	10	50	200	1000
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	2.5	10	50	200	1000
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	2.5	10	50	200	1000
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	2.5	10	50	200	1000
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	2.5	10	50	200	1000
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	2.5	10	50	200	1000
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	2.5	10	50	200	1000
Octachlorodibenzofuran (OCDF)	5	20	100	400	1000
Labeled Analyte	**CS L1** pg/µl	**CS L2** pg/µl	**CS L3** pg/µl	**CS L4** pg/µl	**CS L5** pg/µl
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$--1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$--2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8,9-HpCDF	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
Labeled Clean-up Standard	**CS L1** pg/µl	**CS L2** pg/µl	**CS L3** pg/µl	**CS L4** pg/µl	**CS L5** pg/µl
$^{37}Cl_4$-2,3,7,8-TCDD	.5	2	10	40	200

8.9 47mm Styrene Divinyl Benzene Extraction Disks.

8.10 41gram Styrene Divinyl Benzene Extraction cartridges.

8.11

8.12 Acid Silica Gel Colum. 15mm glass column containing Acidified silica gel and neutral silica gel

8.13 Carbon Column. Ultra clean dual flow carbon column.

8.14 Sodium Thiosulfate.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

Method Blank (MB) - A Method Blank (MB) is required with each extraction batch to confirm that potential background contaminants are not interfering with the identification or quantitation of method analytes. If more than 20 Field Samples are included in a batch, analyze an MB for every 20 samples. If the MB produces a peak within the retention time window of any analyte that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding. Background from method analytes or other contaminants that interfere with the measurement of method analytes must be below 1/2 of the RL.

9.2 Laboratory Control Sample (LCS)

An LCS is required with each extraction batch. The fortified concentration of the LCS must equal to the analyte concentrations in the CS L3 standard. The percent recoveries of the LCS analyses must within the acceptance limits in Table 8. Calculate the percent recovery (%R) for each analyte using the equation

$$\%R = \frac{A \times 100}{B}$$

Where:

A = measured concentration in the fortified sample

B =fortification concentration

Table 8		
Parameter	**LCS Recovery Limits for Aqueous Matrices**	**LCS Recovery Limits for Solid Matrices**
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)	71 – 125	70 - 128
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin (PeCDD)	76 – 121	74 - 135
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	80 – 126	72 - 131
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin (HxCDD)	78 - 134	74 - 134
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin (HxCDD)	76 - 137	71 - 138
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin (HpCDD)	79 - 122	76 - 125
Octachlorodibenzo-*p*-dioxin (OCDD)	81 - 135	73 - 135
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	72 - 138	75 - 135
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	82 - 130	77 - 131
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	77 - 129	75 - 128
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	80 - 130	77 - 130
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	78 - 134	73 - 134
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	83 - 130	74 - 135
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	81 - 130	74 - 133
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	81 - 130	73 - 135
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	77 - 128	72 - 131
Octachlorodibenzofuran (OCDF)	66 - 150	66 - 144

9.3 Initial Calibration Verification (ICV)

Immediately following each initial calibration, analyze a QCS sample from a source different from the source of the CAL standards. If a second vendor is not available, then a different lot of the standard should be used. The QCS should be prepared and analyzed just like a CCV. The respective ion abundances for each analyte must be ± 15% the theoretical ratio. Acceptance criteria for the QCS are identical to the CCVs; the calculated amount for each analyte must be ± 20% of the expected value for unlabeled compounds, and ± 30% for labeled standards. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct.

9.4 Continuing Calibration Verification (CCV)

9.4.1 At the start of each analytical sequence, analyze a midlevel calibration check standard. The CCV should be prepared and analyzed just like a CCV. The respective ion abundances for each analyte must be ± 15% the theoretical ratio. The calculated amount for each analyte must be ± 20% of the expected value for unlabeled compounds, and ± 30% for labeled standards. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedure to locate and correct.

9.4.2 End of run CCV. To be run at the end of each analytical sequence. If the RF for unlabeled standards ≤ 25% RPD and the RF for labeled standards ≤ 35% RPD (relative to the RF established in the ICAL), the mean RF from the two daily CCVs must be used for quantitation of impacted samples instead of the ICAL mean RF value. If the starting and ending CCVRFs differ by more than 25% RPD for unlabeled compounds or 35% RPD for labeled compounds, the sample may be quantitated against a new initial calibration if it is analyzed within two hours.

9.5 Matrix Spike/Matrix Spike Duplicate

9.5.1 Analysis of an MS and MSD is required in each extraction batch and is used to determine that the sample matrix does not adversely affect method accuracy. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, method performance should be established for each. Over time, MS data should be documented by the laboratory for all routine sample sources. The limits listed in table 8 for LCS acceptance are to be used for MS and MSD recoveries. The Percent recovery of each analyte is to be calculated using the calculation:

$$\%R = \frac{(A - B)}{C} \times 100$$

Where:

A = measured concentration in the fortified sample
B = measured concentration in the unfortified sample
C = fortification concentration.

9.5.2 Analysis of an MS and MSD is required in each extraction batch and is used to determine that the sample matrix does not adversely affect method accuracy. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, method performance should be established for each. Over time, MS data should be documented by the laboratory for all routine sample sources. The limits listed in table 6 for LCS acceptance are to be used for MS and MSD recoveries. The Percent recovery of each analyte is to be calculated using the calculation:

$$RPD = \frac{(MS1 - MS2)}{(MS1 + MS2)/2} \times 100$$

Where:

MS1 = measured concentration in the Matrix Spike
MS2 = measured concentration in the Matrix Spike Duplicate

9.6 Laboratory Duplicate

Laboratory Duplicates are to be performed as requested and are project specific. If no project RPD limits are specified, an RPD of ≤ 25% is to be used for all analytes.

9.7 Method-specific Quality Control Samples

Not Applicable

9.8 Method Sequence

- TCDD/TCDF Isomeric resolution check
- CCV with Isomer window check (First/Last eluting)
- MB
- LCS
- MS
- MSD

- Field Samples (n = x)
- Closing CCV

10. Procedure

10.1 Equipment Set-Up

10.1.1 Instrumentation

10.1.1.1 GC Column Performance

Inject a 1 µl aliquot of a column performance check solution (1/20 dilution) containing 2,3,7,8-TCDD and 2,3,7,8-TCDF and the closest eluting isomers (See table 6). The separation of the 2,3,7,8-TCDD and 2,3,7,8-TCDF must be ≤ 25%.

Table 6

Analyte	Concentration (ug/ml)
1,2,3,4-TCDD	.5
1,2,3,7-TCDD and 1,2,3,8-TCDD	.5 (total)
2,3,7,8-TCDD	1.0
1,2,3,9-TCDD	1.0
$^{13}C_{12}$-1,2,3,4-TCDD	.5
$^{13}C_{12}$-2,3,7,8-TCDD	.5
1,3,6,8-TCDF	1.0
2,3,4,7-TCDF	1.0
2,3,7,8-TCDF	2.0
$^{13}C_{12}$-2,3,7,8-TCDF	.5
1,2,3,9-TCDF	1.3
1,2,8,9-TCDF	1.2

10.1.1.2 The mass spectrometer is operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at appropriate masses before any analysis is performed. Static resolving power checks are made and documented.

10.1.1.3 Chromatography time for PCDDs and PCDFs exceeds the long term mass stability of the mass spectrometer. Because the instrument is operated in the high-resolution mode, mass drifts of a few ppm (e.g., 5 ppm in mass) can have serious adverse effects on instrument performance. Therefore, a mass drift correction is mandatory. To that effect, a lock-mass ion from the reference compound is used for tuning the mass spectrometer. The selection of the lock-mass ion is dependent on the masses of the ions monitored within each descriptor. Table 7 shows the lock-mass ions. The level of the reference compound (FC-43) metered into the ion chamber during HRGC/HRMS analyses should be adjusted so that the amplitude of the most intense selected lock-mass ion signal (regardless of the descriptor number) does not exceed 10 percent of

the full scale deflection for a given set of detector parameters. Under those conditions, sensitivity changes that might occur during the analysis can be more effectively monitored.

Table 7

Section 1				
Description	Mass	Time (ms)	Analyte	
	303.90160	98	TeCDF	
	305.987870	98	TeCDF	
Lock	313.983336	3	FC43	
	315.94190	14	$^{13}C_{12}$-TeCDF	
	317.93890	14	$^{13}C_{12}$-TeCDF	
	319.89650	98	TeCDD	
	321.89360	98	TeCDD	
	327.88470	98	$^{37}Cl_4$-TeCDD	
	331.93680	14	$^{13}C_{12}$-TeCDD	
	333.93390	14	$^{13}C_{12}$-TeCDD	
	339.93390	98	PeCDF	
	341.85620	98	PeCDF	
Cali	363.98017	3	FC43	
	375.83640	14	HxCDPE	
Section 2				
Description	Mass	Time (ms)	Analyte	
Lock	313.98336	3	FC 43	
	339.85970	104	PeCDF	
	341.85670	104	PeCDF	
	351.90000	15	$^{13}C_{12}$-PeCDF	
	353.89700	15	$^{13}C_{12}$-PeCDF	
	355.85460	104	PeCDD	
	357.85160	104	PeCDD	
Cali	363.98017	3	FC43	
	367.89433	15	$^{13}C_{12}$-PeCDF	
	369.89138	15	$^{13}C_{12}$-PeCDF	
	373.82018	104	HxCDF	
	375.81723	104	HxCDF	
	409.79740	15	HpCDE	
Section 3				
Description	Mass	Time (ms)	Analyte	
	373.82080	152	HxCDF	
	375.81780	152	HxCDF	
Lock	375.97974	5	FC43	
	383.86390	21	$^{13}C_{12}$-HxCDF	
	385.86100	21	$^{13}C_{12}$-HxCDF	
	389.81570	152	HxCDD	
	391.81270	152	HxCDD	
	401.85590	21	$^{13}C_{12}$-HxCDF	
	403.85290	21	$^{13}C_{12}$-HxCDF	
Cali	413.97698	5	FC43	
	445.75550	21	OCDPE	

Section 4				
Description	Mass	Time (ms)	Analyte	
	407.78180	154	HpCDF	
	409.77890	154	HpCDF	
Lock	413.97698	4	FC43	
	417.82530	22	$^{13}C_{12}$-HpCDF	
	419.82200	22	$^{13}C_{12}$-HpCDF	
	423.77660	154	HpCDD	
	425.77370	154	HpCDD	
	435.81690	22	$^{13}C_{12}$-HpCDF	
	437.81400	22	$^{13}C_{12}$-HpCDF	
Cali	463.97378	4	FC43	
	479.71650	22	NCDPE	
Section 5				
Description	Mass	Time (ms)	Analyte	
Lock	425.97681	4	FC43	
	441.74280	179	OCDF	
	443.73990	179	OCDF	
	457.73770	179	OCDD	
	459.73480	179	OCDD	
Cali	463.97378	4	FC32	
	469.77500	25	$^{13}C_{12}$-OCDF	
	471.77500	25	$^{13}C_{12}$-OCDF	
	513.67750	25	DCCPE	

10.1.1.4 The mass spectrometer tuning conditions are based on the groups of monitored ions shown in Table 7. By using a FC43 molecular leak, tune the instrument to meet the minimum required resolving power of 10,000 (10 percent valley) at m/z 313.98336 (FC43). By using peak matching conditions and the aforementioned FC43 reference peak, verify that the exact mass of m/z 463.97378 (FC43) is within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage jump performed in any of the five mass descriptors (Table 7).

10.2 Initial Calibration

10.2.1 At a minimum, all five high-resolution concentration calibration solutions listed in Table 5 must be used for the initial calibration.

10.2.2 Tune the instrument with FC43, as described in Sec. 10.1.1.4.

10.2.3 Inject 1 µL of the GC column performance check solution (Sec. 10.1.1.1) and acquire SIM mass spectral dat. The total cycle time must be < 1 sec. The laboratory must not perform any further analysis until it is demonstrated and documented that the criteria listed in Sec 9.1 were met.

10.2.4 By using the same GC and MS conditions that produced acceptable results with the column performance check solution, analyze a 1-µL portion of each of the five concentration calibration solutions once with the following mass spectrometer operating parameters.

10.2.5 The ratio of integrated ion current for the ions appearing in Table 7 (homologous series quantitation ions) must be within the indicated control limits, ± 15%.

10.2.6 For each selected ion current profile (SICP) and for each GC signal corresponding to the elution of a target analyte and of its labeled standards, the signal-to-noise ratio (S/N) must be better than or equal to 10.

10.2.7 Calculate the 17 relative response factors (RF) for unlabeled target analytes relative to their appropriate internal standards and the fifteen RFs for the $^{13}C_{12}$-labeled internal standards relative to the two recovery standards according to the following formulae:

$$RF_n = \frac{(A_n^1 + A_n^2) \times Q_{is}}{(A_{is}^1 + A_{is}^2) \times Q_n}$$

$$RF_{is} = \frac{(A_{is}^1 + A_{is}^2) \times Q_{rs}}{(A_{rs}^1 + A_{rs}^2) \times Q_{is}}$$

Where:

A_n^1 and A_n^2 = sum of the integrated ion abundances of the quantitation ions for unlabeled PCDDs/PCDFs.

A_{is}^1 and A_{is}^2 = sum of the integrated ion abundances of the quantitation ions for labeled internal standards.

A_{rs}^1 and A_{rs}^2 = sum of the integrated ion abundances of the quantitation ions for labeled recovery standards.

Q_{is} = quantity of the internal standard injected (pg)

Q_{rs} = quantity of the recovery standard injected (pg)

Q_n = quantity of the unlabeled PCDD/PCDF injected (pg)

10.2.8 Calculate the mean RF values and their respective percent relative standard deviations (%RSD) for the five calibration solutions:

$$\text{Average } RF_n = {}^{5}\sum_{j=n} 1RF_{n(j)}/5$$

where n represents a particular PCDD/PCDF (2,3,7,8-substituted) congener (n = 1 to 17), and j is the injection number (or calibration solution number; j = 1 to 5).

10.2.9 The relative response factors to be used for the determination of the concentration of total isomers in a homologous series are calculated as follows:

For congeners that belong to a homologous series containing only one isomer (e.g., OCDD and OCDF) or only one 2,3,7,8-substituted isomer (Table 4; TCDD, PeCDD, HpCDD, and TCDF), the RF used will be the same as the RF determined in Sec. 10.8.8.

For congeners that belong to a homologous series containing more than one 2,3,7,8-substituted isomer (Table 4), the RF used for those homologous series will be the mean of the RFs calculated for all individual 2,3,7,8-substituted congeners using the equation below:

$$\text{Average } RF_k = {}^{t}\sum_{n=1} 1RF_n/t$$

where:

k = PeCDF, HxCDF, HxCDD, HpCDF

t = total number of 2,3,7,8-substituted isomers present in the calibration solutions for each homologous series (PeCDF (2 isomers), HxCDF (4 siomers), HxCDD (3 Isomers) HpCDF (2 Isomers).

10.2.10 Relative response factors (RF_m) to be used for the determination of the percent recoveries for the 15 internal standards are calculated as follows:

$$RF_m = A_{IS} \text{ X } Q_{rs} / Q_{is} \text{ X } A_{rs}$$

$$\text{Average } RF_m = = {}^{5}\sum_{j=1} 1RF_{m(j)}/5$$

Where:

m = congener type and j = 1 to 5 (injection number)

A_{is} = sum of the integrated ion abundances of the quantitation ions for a given internal standard.

A_{rs} = sum of the integrated ion abundances of the quantitation ions for the appropriate recovery standard.

Q_{rs}, Q_{is} = quantities of, respectively the recovery standard and particular internal standards injected (pg).

RF_m = relative response factor of a particular internal standard (m) relative to an appropriate recovery standard as determined from one injection.

Average RF_m = calculated mean relative response factor of a psrticular internal standard (m) relative to an appropriate recovery standard, as determined from the five initial calibration injections (j).

10.2.11 The percent relative standard deviations for the mean response factors from the 17 unlabeled standards must not exceed ± 20 percent, and those for the nine labeled reference compounds must not exceed ± 20 percent.

10.2.12 The S/N for the GC signals present in every SICP (including the ones for the labeled standards) must be $\geq$ 10.

10.2.13 The ion abundance ratios must be ± 15%

10.3 Equipment Operation and Sample Processing

10.3.1 Sample Preparation

The sample fortification solution containing the carbon-labeled internal standards is added to each sample prior to extraction.

For soils, sediments and other solid matrices, an aliquot of 20 µl is added to the sample (typically 10 grams) using a 20µl disposable tip auto pipette.

For aqueous matrices, because the fortification solution is in nonane, an aliquot of 1 ml of acetone is prepared and 20 µl of the fortification solution is spiked into the acetone. The acetone is then transferred to the aqueous sample (typically 500 ml to 1 L).

It has been observed that making secondary solution of the nonane based fortification solution into acetone is prone to evaporation loss and analyte concentration. It is thus not recommended to make working solutions in acetone for extended usage.

For laboratory blanks and control spikes in tissue matrices, due to the unavailability of tissue matrices free of target analytes, 1 gram of a clean reference oil will be added to the extraction media to simulate the lipid content of an approximate 10 gram sample.

If sample is an LCS or MS/MSD, a 5 µl aliquot of the native PAR solution is added to the sample in the same manner as the fortification solution.

10.3.1.1 Extraction of Soil, Sediment, Tissues and solid matrices by Microwave Extraction.

10.3.1.1.1 Transfer the prepared sample aliquot of sample containing the fortification solution to a 75 ml microwave extraction vessel.

10.3.1.1.2 Add an appropriate amount of Sodium Sulfate to the vessel; typically, 20 grams. It is important that a relatively equal quantity of sodium sulfate be added to each vessel.

10.3.1.1.3 Add 35 mls of Toluene to each vessel, cap and gently mix the cell by inverting it several times.

10.3.1.1.4 Arrange the cells in an equal manner on the microwave carrousel and initiate the extraction program. The extraction program is as follows:

Extraction Temperature: 110 °C

Extraction Static Time: 20 minutes

Cool Time: 20 minutes

10.3.1.1.5 After extraction, the contents of each extraction vessel is to be passed through a glass funnel containing a 150 mm sheet of filter paper into an appropriate sized evaporation vessel.

10.3.1.1.6 Rinse the extraction vessel with an additional 10 mls of toluene and passes through the filter.

10.3.1.2 Extraction of Soil, Sediment, Tissues and solid matrices by Soxhlet Extraction

10.3.1.2.1 Mix the prepared sample aliquot of sample containing the fortification solution with 20 grams of sodium sulfate using a metal spatula. Sample should be free flowing with no visible clumps.

10.3.1.2.2 Transfer the sample to the Soxhlet apparatus on top of a glass wool plug.

10.3.1.2.3 Add 200 mls of Toluene to a 250 ml round bottom flask and reflux the sample for 16 hours. The solvent must cycle through the system 5 times per hour.

10.3.1.2.4 Cool and filter the extract passed through a glass funnel containing a 150 mm sheet of filter paper into an appropriate sized evaporation vessel.

10.3.1.2.5 Rinse the extraction vessel with an additional 10 mls of toluene and passes through the filter.

10.3.1.3 Extraction of Aqueous Samples by Solid Phase Extraction.

10.3.1.3.1 Place a 47mm extraction disk in a disk holder/cartridge affixed on a vacuum manifold apparatus.

10.3.1.3.2 Mark the water level on the side of the sample bottle.

10.3.1.3.3 Adjust the sample pH to <2 by adding 1:1 HCl drop wise to the fortified aqueous sample.

10.3.1.3.4 When the sample is judged to contain 1 percent or more solids, the sample must be filtered through a glass fiber filter that has been rinsed with toluene. If the suspended solids content is too great to filter through the 0.45µm filter, centrifuge the sample, decant, and then filter the aqueous phase.

10.3.1.3.5 Combine the solids from the centrifuge bottle(s) with the particulates on the filter and with the filter itself and proceed with the microwave extraction in section 10.2

10.3.1.3.6 Rinse the SPE disk with 10 mls of toluene, letting soak for 1 minute.

10.3.1.3.7 With the vacuum pump running at a setting of ~10 mmHG, open the valve and completely drain the toluene from the disk. Repeat with 2 more cycles of toluene.

10.3.1.3.8 Rinse the disk with 10 mls of methanol, letting soak for 1 minute.

10.3.1.3.9 Under the same conditions of step 10.3.1.3.7, open the valve to allow the methanol to drain at ~5 ml/min. When the level of the methanol is near the level of the disk, close the valve. Do not allow the disk to go completely dry.

10.3.1.3.10 Repeat step 10.3.1.3.9 two more times.

10.3.1.3.11 Following the procedure in steps 10.3.1.3.8 through 10.3.1.3.10, repeat with 3 cycles of reagent water.

10.3.1.3.12 Fill the sample cup with the sample by pouring it from the sample container. Open the valve and allow to drain at a rate of ~20 ml/min. Continue to add sample to the cup till all the sample is consumed, not allowing the disk to go dry till all the sample has passed through the disk.

10.3.1.3.13 Allow the disk to dry by pulling air across the disk for 10 minutes.

10.3.1.3.14 After drying, close the valve. Rinse the sample container with 5 ml acetone and transfer the toluene to the disk, allowing to soak for 1 minute.

10.3.1.3.15 Open the valve and at a flow rate of ~10 ml/min, allow the acetone to drain into a collection vial.

10.3.1.3.16 Rinse the sample container with 10 ml toluene and transfer the toluene to the disk, allowing to soak for 1 minute.

10.3.1.3.17 Open the valve and at a flow rate of ~10 ml/min, allow the toluene to drain into a collection vial

10.3.1.3.18 Repeat step 10.3.1.3.16 with two more cycles of toluene, allowing the disk to completely drain after the last step.

10.3.1.3.19 Pass the extract through a glass funnel containing 5-7 grams of sodium sulfate containing and a 150 mm sheet of filter paper into an appropriate sized evaporation vessel.

10.3.1.3.20 Re-fill the sample bottle to the marked meniscus line with water. Pour the water into a Class A graduated cylinder and record the sample volume extracted.

10.3.2 Sample Concentration

10.3.2.1 After sample extraction, all extracts are to be evaporated in a nitrogen assisted water bath at 50 °C. The nitrogen should be introduced at 8-10 PSI.

10.3.2.2 Evaporate each sample down to < 1ml.

10.3.2.3 Add 1 ml of dodecane to each sample and reduce back to 1 ml to remove all residual extraction solvent. It is essential the extract be free of any methylene chloride or toluene used in extraction.

10.3.2.4 Add an additional 1 ml of hexane to the extract bringing the final volume to 2 mls.

10.3.2.5 Cap and store in a 4 ml amber vial at ambient temperature till extract clean-up step.

10.3.3 Sample Extract Clean-up

10.3.3.1 Attach Acid silica columns to the sample rack, above empty 60ml collection vials.

10.3.3.2 Add 10 mls of hexane to each silica column and allow to flow via gravity until hexane begins to drip from the columns.

10.3.3.3 Use a Pasteur pipette to fill the square end of each carbon mini column with hexane, and attach carbon mini-columns twisting the square cut end firmly onto tip of acid silica columns while dripping hexane. Flow should stop with addition of carbon mini column.

10.3.3.4 Using a lure fitted manifold at < 10 PSI of nitrogen, add 5 mls hexane to the silica column using a needle funnel and pressurize the columns.

10.3.3.5 Allow hexane to flow through the columns at a rate of about .5-2 ml/min. Close the valve stopping flow when the solvent layer is 2-5 mm from the head of the silica layer. Do not allow the top of the column to go dry.

10.3.3.6 Add 25 µl of clean-up standard to each sample extract.

10.3.3.7 Using the needle funnels, add the sample extract to the silica column.

10.3.3.8 Open the valve to load the extract onto the silica column, closing the valve and stopping flow .5-2 mm above the top of the silica layer.

10.3.3.9 Rinse the sample vial with an additional 2 ml of hexane and repeat steps 10.3.3.7 to 10.3.3.8.

10.3.3.10 Add 10 mls of hexane to the acid silica columns and continue to elute columns at .5-2 ml/min, stopping with the solvent 2-5 mm from the silica layer.

10.3.3.11 Repeat step 10.3.3.10 two more times for a total of 30 mls, allowing on the final wash only, for air to penetrate the acid layer till it reaches the neutral silica, about 1-2 cm from the bottom of the column. Do not allow the air to reach the carbon column.

10.3.3.12 Remove the acid silica column and attach the mini-carbon column to an empty glass column. Discard the silica columns.

10.3.3.13 Add 6 ml of 1:1 hexane:toluene to the carbon columns and allow to elute stopping the flow when the solvent layer reached the tip of the Teflon sleeve of the mini carbon column.

10.3.3.14 Remove the mini carbon columns, reverse (invert) the column and attach the slanted sleeve end to the reservoir.

10.3.3.15 Add 15 mls of toluene and elute into an evaporation flask till the last drop of toluene is eluted from the carbon column.

10.3.3.16 Transfer the extracts to the nitrogen assisted water bath and reduce the extract till the volume is < 1ml.

10.3.3.17 Transfer the extract to a micro GC vial containing 10 µl of nonane.

10.3.3.18 Under a gentle stream of nitrogen, reduce the solvent until the solvent volume is at the level of the nonane (about ½ way up the micro portion of the vial.

10.3.3.19 Remove from vials, add 10 µl of recovery internal standard, cap and transfer for HRMS analysis.

10.3.4 High-Resolution GC/MS Analysis

10.3.4.1 For 2,3,7,8-substituted congeners, which have an isotopically-labeled internal or recovery standard present in the sample extract, the retention time (RRT; at maximum peak height) of the sample components must be within -1 to +3 sec of the isotopically-labeled standard.

10.3.4.2 For 2,3,7,8-substituted compounds that do not have an isotopically-labeled internal standard present in the sample extract, the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration. Identification of OCDF is based on its retention time relative to $^{13}C_{12}$-OCDD as determined from the daily routine calibration results.

10.3.4.3 For non-2,3,7,8-substituted compounds (tetra through octa; totaling 119 congeners), the retention time must be within the corresponding homologous retention time windows established by analyzing the column performance check solution.

10.3.4.4 The ion current responses for both ions used for quantitative purposes must reach maximum simultaneously (± 2 sec).

10.3.4.5 The integrated ion currents for the two ions used for quantitation purposes must have a ratio of ± the theoretical ratios.

10.3.4.6 All ion currents intensities must be ≤ 2.5 times noise level for positively identification of an unlabeled PCDD/PCDF compound or group of coeluting isomers. Labeled analytes must be ≥ 10 times.

10.3.4.7 Polychlorinated diphenyl ether interferences can inhibit the detection of PCDFs. For each level of chlorination, the respective PCDPE chlorination level shall also be monitored.

10.4 Continuing Calibration

10.4.1 Routine calibration (continuing calibration check) -- Routine calibrations must be performed at the beginning of a 12-hr period, after successful mass resolution and GC resolution performance checks. A routine calibration is also required at the end of a 12-hr shift. Inject 1 µL of the concentration calibration solution CS L3 standard.

10.4.2 The measured RFs [RF_n for the unlabeled standards] obtained during the routine calibration runs must be within ± 20 percent of the mean values established during the initial calibration.

10.4.3 The measured RFs [RF_m for the labeled standards] obtained during the routine calibration runs must be within ± 30 percent of the mean values established during the initial calibration.

10.4.4 The ion abundance ratios must be within the allowed control limits ± 15%.

10.5 Preventive Maintenance

All repair and non-routine maintenance records including outside service visits are maintained in the instrument maintenance logbooks.

Injection Port Maintenance: Maintenance should be done when the daily CCAL starts to demonstrate performance degradation. The type of samples analyzed will have an effect on how soon maintenance should be performed. Septum Maintenance: The septum needs to be changed approximately every two-hundred injections. Unscrew the top septum nut, remove the pierced septum, and replace with a new 11mm Thermolite green septum. Screw the top septum nut back on.

Column Maintenance: Maintenance should be done when the daily CCAL starts to demonstrate degradation. The type of samples analyzed will have an effect on how soon maintenance should be performed. Generally maintenance is performed by trimming 6 cm off the front of the column. The column is then installed into the injection port liner, and the inlet nut is tightened.

11. Data Evaluation, Calculations and Reporting

11.1 For gas chromatographic peaks that have met the all criteria, calculate the concentration of the PCDD or PCDF compounds using the formula:

$$C_x = \frac{A_x \text{ X } Q_{is}}{A_{is} \text{ X W X Average } RF_n}$$

Where:
C_x = concentration of unlabeled PCDD/PCDF congeners (or group of coeluting isomers within a homologous series) in pg/g,

A_x = sum of the integrated ion abundances of the quantitation ions for unlabeled PCDDs/PCDFs,

A_{IS} = sum of the integrated ion abundances of the quantitation ions for the labeled internal standards

Q_{IS} = quantity, in pg, of the internal standard added to the sample before extraction

W = weight, in g, of the sample (solid or organic liquid), or volume in mL of an aqueous sample,

Average RF_n = calculated mean relative response factor for the analyte

11.2 Calculate the percent recovery of the internal standards measured in the sample extract, using the formula:

$$\text{Percent Recovery} = \frac{A_{IS} \text{ X } Q_{rs}}{Q_{IS} \text{ X } A_{RS} \text{ x Avg. } RF_m} \text{ X100}$$

Where:
A_{IS} = sum of the integrated ion abundances of the quantitation ions for the labeled internal standards

A_{rs} = sum of the integrated ion abundances of the quantitation ions for the appropriate recovery standard.

Q_{IS} = quantity, in pg, of the internal standard added to the sample before extraction

Q_{rs} = quantities of the recovery standard added to the extract (pg).

Avg. RF_m = calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard.

11.3 If a smaller sample size would not be representative of the entire sample, one of the following options is recommended:

- Re-extract an additional aliquot of sufficient size to insure that it is representative of the entire sample. Spike it with a higher concentration of internal standard. Prior to GC/MS analysis, dilute the sample so that it has a concentration of internal standard equivalent to that present in the calibration standard. Then, analyze the diluted extract.
- Re-extract an additional aliquot of sufficient size to insure that it is representative of the entire sample. Spike it with a higher concentration of internal standard. Immediately following extraction, transfer the sample to a volumetric flask and dilute to known volume. Remove an appropriate aliquot and proceed with cleanup and analysis.
- Use the original analysis data to quantitate the internal standard recoveries. Respike the original extract (note that no additional cleanup is necessary) with 100 times the usual quantity of internal standards. Dilute the re-spiked extract by a factor of 100. Reanalyze the diluted sample using the internal standard recoveries calculated from the initial analysis to correct the results for losses during isolation and cleanup.

11.4 The total concentration for each homologous series of PCDD and PCDF is calculated by summing up the concentrations of all positively identified isomers of each homologous series. Therefore, the total should also include the 2,3,7,8-substituted congeners. The total number of GC signals included in the homologous total concentration value must be specified in the report. If an isomer is not detected, use zero in this calculation.

11.5 Sample specific estimated quantitation limit -- The sample specific estimated quantitation limit (EQL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. An EQL is calculated for each 2,3,7,8-substituted congener that is not identified, regardless of whether or not other non-2,3,7,8-substituted isomers are present. Two methods of calculation can be used, as follows, depending on the type of response produced during the analysis of a particular sample.

- Samples giving a response for both quantitation ions (Tables 6 and 9) that is less than 2.5 times the background level.

Use the expression below to calculate an EDL for each 2,3,7,8 unsubstituted PCDD/PCDF that does <u>not</u> have a response with S/N ≥ 2.5. The background level is determined by measuring the range of the noise (peak to peak) for the two quantitation ions of a particular 2,3,7,8-substituted isomer within an homologous series, in the region of the SICP trace corresponding to the elution of the internal standard (if the congener possesses an internal standard) or in the region of the SICP where the congener is expected to elute by comparison with the routine calibration data (for those congeners that do not have a ^{13}C-labeled standard), multiplying that noise height by 2.5, and relating the product to an estimated concentration that would produce that peak height. Use the formula:

$$EQL = \frac{2.5 \times H_x \times Q_{IS}}{H_{is} \times W \times Avg\ RF_n}$$

Where:

EQL = estimated quantitation limit for homologous 2,3,7,8-substituted PCDDs/PCDFs.

H_x = sum of the height of the noise level for each quantitation ion for the unlabeled PCDDs/PCDFs

H_{is} = sum of the height of the noise level for each quantitation ion for the labeled internal standard

W = calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard.

Q_{is} = quantity, in pg, of the internal standard added to the sample before extraction

Avg RF_n = calculated mean relative response factor for the labeled internal standard relative to the appropriate recovery standard.

• Estimated maximum possible concentration -- An estimated maximum possible concentration (EMPC) is calculated for 2,3,7,8-substituted isomers that are characterized by a response with an S/N of at least 2.5 for both the quantitation ions, and meet all of the identification criteria except the ion abundance ratio criteria or when a peak representing a PCDPE has been detected. An EMPC is a worst-case estimate of the concentration. Calculate the EMPC according to the expression shown in Sec. 11.1.

11.6 The 2,3,7,8-TCDD toxicity equivalents (TE) of PCDDs and PCDFs present in the sample are calculated, if requested by the data user, according to the method recommended by the Chlorinated Dioxins Workgroup (CDWG) of the EPA and the Center for Disease Control (CDC). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) to each of the fifteen 2,3,7,8-substituted PCDDs and PCDFs and to OCDD and OCDF. The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by summing the TEF times their concentration for each of the compounds or groups of compounds listed in Table 9.

Table 9

Analyte	TEF
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	1.0
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	.5
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	.1
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	.1
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)	.1
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)	.01
Octachlorodibenzo-p-dioxin (OCDD)	.001
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	.1
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	.05
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	.5

1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	.1
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	.1
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	.1
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	.1.
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	.01
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	.01
Octachlorodibenzofuran (OCDF)	.001

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

Holding time exceedance, improper preservation and observed sample headspace are noted on the nonconformance report form.

When analysis of samples indicates possible extraction problems, such as poor surrogate recoveries, poor LCS/MS/MSD recoveries, or suspected contamination in blanks or samples, re-extractions are required. Depending on the particular failure, the re-extraction may be of a specific sample or the entire extraction batch.

The analyst that determines the need for re-extraction must fill out a sample re-extract request form. This form notes the reason for the re-extraction request along with any special requirements, and the date and time that the re-extract is needed. Re-extraction request forms are maintained on file to help track the cause for re-extractions, and to be used as a tool in improving systems to minimize the need for re-extractions.

Depending on the results of the re-extraction, the first, second, or both sets of results may be reported to the client, along with a narrative report detailing the problems encountered and the resolution.

If non-compliant organic compound results are to be reported, the Semi Volatile Organics Department Manager, the Laboratory Director, and/or the QA Officer must approve the reporting of these results. The laboratory Project Manager shall be notified, and may choose to relay the noncompliance to the client, for approval, or other corrective action, such as re-sampling and reanalysis. The analyst or Department Manager performing the secondary review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

13. Method Performance

13.1 Detection Limit Study (DL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the DL, LOD, and/or LOQ as outlined in Alpha SOP ID 1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP ID 1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Hazardous Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP ID 1732 Detection Limit (DL), Limit of Detection (LOD) & Limit of Quantitation (LOQ) SOP

SOP ID 1739 Demonstration of Capability (DOC) Generation SOP

SOP ID 1728 Hazardous Waste Management and Disposal SOP

16. Attachments

None.

Analysis of

Chlorinated Herbicides by GC Using Methylation Derivatization

Reference Methods: **EPA 8151A,** SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, 1997.

MA BWSC-CAM Section VC, Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 8151A, for the Massachusetts Contingency Plan (MCP). Revision 2. May 28, 2004.

1. Scope and Application

Matrices: Aqueous, soil and waste.

Definitions: See Alpha Laboratories Quality Manual Appendix A

Specifically, Method 8151A may be used to determine the following compounds:

Parameter	CAS No.[a]	MOL WT.	WT as methyl ester	Conversion Factor
2,4-D [1, 2, 3]	94-75-7	221.04	235.06	0.94
2,4-DB	94-82-6	326.18	340.18	0.96
2,4,5-TP (silvex) [1, 2, 3]	93-72-1	269.51	283.51	0.95
2,4,5-T [1, 2]	93-76-5	255.48	269.48	0.95
Dalapon	75-99-0	142.96	156.96	0.91
Dicamba	1918-00-9	221.04	235.04	0.94
Dichloroprop	120-36-5	235.06	249.06	0.94
Dinoseb	88-85-7	240.21	254.21	0.95
MCPA	94-74-6	200.62	214.62	0.93
MCPP	93-65-2	214.65	228.65	0.94

[a] Chemical Abstract Service Registry Number

[1] RCRA List

[2] APA List

[3] TCLP List

Method 8151A is a capillary gas chromatographic (GC) method for determining certain chlorinated acid herbicides and related compounds in aqueous, soil and waste matrices.

Because these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), Method 8151A describes a hydrolysis step than can be used to convert herbicide esters into the acid form prior to analysis. Herbicide esters generally have a half-life of less than one week in soil.

When Method 8151A is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. Section 9.4.9 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

The estimated detection limits for each of the compounds in aqueous and soil matrices are listed in Table 1. The detection limits for a specific waste sample may differ from those listed, depending upon the nature of the interferences and the sample matrix.

The following compounds may also be determined using this method:

Parameter	CAS No.[a]	MOL WT.	WT as methyl ester	Conversion Factor
Acifluorfen	50594-66-6	361.66	375.66	0.96
Bentazon	25057-89-0	240.28	254.28	0.94
Chloramben	133-90-4	206.02	220.02	0.93
DCPA diacid[b]	2136-79-0	303.91	317.91	0.95
3,5-Dichlorobenzoic acid	51-36-5	191.01	205.01	0.93
Picloram	1918-02-1	241.46	255.46	0.94
4-Nitrophenol	100-02-1	139.10	153.10	0.91
Pentachlorophenol	87-86-5	266.34	280.34	0.95

[a] Chemical Abstract Service Registry Number

[b] DCPA monoacid and diacid metabolites included in method scope;
DCPA diacid metabolite used for validation studies.
DCPA is a dimethyl ester.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and skilled in the interpretation of gas chromatograms. Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic). Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability..

2. Summary of Method

This SOP for Method 8151A details gas chromatographic conditions for the analysis of chlorinated acid herbicides in water, soil, and waste samples. The hydrolysis of esters is also described.

Water, soil, and waste samples are extracted with diethyl ether and then derivitized with diazomethane. The derivatives are determined by gas chromatography with an electron capture detector (GC/ECD). The results are reported as acid equivalents.

Herbicide esters are determined using this method. Hydrolysis conditions for the esters in water and soil extracts are described.

3. Reporting Limits

The sensitivity of Method 8151A depends on the level of interferences, in addition to instrumental limitations. Table 1 lists the estimated GC/ECD detection limits that can be obtained in aqueous and soil matrices in the absence of interferences. Detection limits for a typical waste sample should be greater.

4. Interferences

4.1 Refer to Method 8000 for instrumental interferences.

4.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks.

4.2.1 Glassware must be scrupulously cleaned. Clean each piece of glassware as soon as possible after use by rinsing it with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap water, then with organic-free reagent water. Glassware should be solvent-rinsed with acetone and pesticide-quality hexane. After rinsing and drying, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store glassware inverted or capped with aluminum foil. Immediately prior to use, glassware should be rinsed with the next solvent to be used.

4.2.2 The use of high purity reagents and solvents helps to minimize interference problems.

4.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

4.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure.

4.5 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids.

4.6 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

4.7 Sample extracts must be dry prior to methylation otherwise poor recoveries will be obtained.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.1 Lab coats, safety glasses, and gloves must be worn when handling supplies, samples, extracts, standards or solvents, and when washing glassware.

5.2 All extract concentration steps must be performed in extraction hoods. All solvent and extract transfers must also be handled in a hood.

5.3 All expired stock standards, working standards, and spent sample extracts must be placed into the waste bucket in the laboratory for future disposal by the Hazardous Waste Manager. The container must be properly labeled with hazard warning labels indicating the container contents.

5.4 Bottles containing flammable solvents must be stored in the flammables cabinet or in the vented cabinets found under the hoods. All ether bottles are to be checked for peroxide immediately upon opening.

5.5 All waste solvents must be transferred to the satellite waste storage containers located in the extraction laboratory. Separate containers are provided for chlorinated and non-chlorinated solvents and must be used accordingly. Under no circumstances are solvents to be poured down the sink drains.

5.6 Inspect all glassware prior to use. Do not use any glassware that is chipped or cracked if it could present a safety hazard. Damaged glassware is put aside for repair; otherwise the piece is discarded. A number is etched onto each KD concentrator tube to keep track of calibration (Refer to SOP/08-04, KD Tube Calibration).

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Aqueous samples are collected in two one-liter amber glass containers. Soil samples are collected in 8oz. glass jars.

6.2 Sample Preservation

Both aqueous and soil/solid samples are stored in refrigerators to maintain a temperature of 2 – 6 °C.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Both aqueous and soil/solid samples and extracts are stored under refrigeration (2 – 6 ºC) and protected from light. Aqueous samples must be extracted within 7 days from the time of collection; soil samples, within 14 days from collection. Sample extracts must be analyzed within 40 days following extraction.

After the extraction is completed, the sample extract is stored in a stoppered KD tube before being transferred to a crimp-top or screw cap vial for analysis and long-term storage.

7. Equipment and Supplies

7.1 Gas Chromatograph, Hewlett Packard 6890: An analytical system complete with gas chromatograph configured for split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and data system.

7.2 GC Columns: Alpha utilizes dual-column analyses. The dual-column approach involves either a single injection that is split between two columns that are mounted in a single gas chromatograph, or dual injections of the split extract on a single GC equipped with two columns. Typical column pairs used are listed below. Other columns may be used as long as method performance criteria can be met.

7.2.1 Narrow Bore Column Pair

Column 1: 30m x 0.32mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5, or equivalent), 0.25µm film thickness.

Column 2: 30m x 0.32mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent) 0.25µm film thickness.

7.2.2 Alternate Column Pair

Column 1: STX-CLP 30m x 0.32mm 0.32 um film thickness
Column 2: STX-CLPII 30m x 0.32mm ID 0.25um film thickness

8. Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4±2 °C in Teflon(R)-sealed containers in the dark. When a large volume of standard is prepared, aliquots of that lot are stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC tests indicate a problem. All other standard solutions must be replaced after six months or sooner if routine QC indicates a problem.

8.1 Reagent water: All references to water in this method refer to reagent water from Alpha's DI water treatment system.

8.2 Stock Standard Solutions: All stock standard solutions are purchased from commercial vendors as ampulated certified solutions. When an ampulated stock solution is opened, it is transferred to a labeled amber screw-cap vial. The expiration date of the stock solution is either the vendor specified expiration date, or 1 year from the date the ampule was opened, whichever is sooner. Typical stock standard concentrations are listed in Table 2

8.2.1 Internal Standard Stock Solution: 4,4'-dibromooctafluorobiphenyl (DBOB), 250 µg/mL in Acetone. Purchased commercially prepared by AccuStandard, Cat # M-8151-IS.

8.2.2 Primary Calibration Stock Standards (Initial Calibration)

8.2.2.1 2,4-Dichlorophenyl acetic acid (DCAA) methyl ester solution: 100µg/mL in Acetone. Purchased commercially prepared by Ultra Scientific, Cat # PPS-166.

8.2.2.2 Methylated Herbicides Mixture: 100 µg/mL in Methanol (except for MCPP and MCPA at 10000µg/mL). Purchased commercially prepared by Ultra Scientific, Cat # HBM-8151M.

8.2.3 Secondary Calibration Stock Standards (Continuing Calibration)

8.2.3.1 2,4-Dichlorophenyl acetic acid (DCAA) methyl ester solution: 100µg/mL in MTBE. Purchased commercially prepared by Accustandard, Cat # M515-SS.

8.2.3.2 Chlorinated Herbicides Methyl Derivatives: 100µg/mL in MTBE (except for MCPP and MCPA at 10000µg/mL. Purchased commercially prepared by Accustandard, Cat # M-8151.

8.2.4 Spiking Stock Standards

8.2.4.1 Surrogate Stock: 2,4-Dichlorophenyl acetic acid (DCAA) {underivatized}, 100µg/mL in Acetone. Purchased commercially prepared by AccuStandard, Cat # M8150B-SS.

8.2.4.2 LCS/MS Stock: Underivatized Chlorinated Herbicides, 100µg/mL in Acetone (except for MCPP and MCPA at 10000µg/mL). Purchased commercially prepared by AccuStandard, Cat # M8151A.

8.3 Calibration Standards: Calibration standards are prepared volumetrically by diluting the appropriate vendor derivatized stock standard(s) (Sections 8.2.2 and 8.2.3) with Hexane. Calibration standards expire 6 months from the date of preparation, or on the earliest expiration date of any of the stock solutions used to prepare the calibration standard. Calibrations are performed at the 6 concentration levels listed in Table 2.

8.3.1 ICAL Surrogate Stock Standard: To a 10mL volumetric flask, add 1mL of DCAA Methyl Ester Solution (Section 8.2.2.1). Bring to volume with Hexane. Final concentration is 10µg/mL.

8.3.2 Intermediate Initial Calibration Standard: To a 10mL volumetric flask, add 1mL of each stock standard listed in Section 8.2.2. Bring to volume using Acetone and Hexane. Final concentration is 10µg/mL for all analytes except MCPP and MCPA at 1000µg/mL.

8.3.2.1 Working Initial Calibration Standards

8.3.2.1.1 Cal Level 1: To a 10mL volumetric flask, add 50µL of Intermediate Initial Calibration Standard (Section 8.3.2) and 50µL of ICAL Surrogate Stock Standard (Section 8.3.1). Bring to volume with Hexane. Final concentration is 0.05µg/mL for all analytes except MCPP and MCPA at 5.0µg/mL.

8.3.2.1.2 Cal Level 2: To a 10mL volumetric flask, add 100µL of Intermediate Initial Calibration Standard (Section 8.3.2) and 100µL of ICAL Surrogate Stock Standard (Section 8.3.1). Bring to volume with Hexane. Final concentration is 0.10µg/mL for all analytes except MCPP and MCPA at 10.0µg/mL.

8.3.2.1.3 Cal Level 3: To a 10mL volumetric flask, add 200µL of Intermediate Initial Calibration Standard (Section 8.3.2) and 200µL of ICAL Surrogate Stock Standard (Section 8.3.1). Bring to volume with Hexane. Final concentration is 0.20µg/mL for all analytes except MCPP and MCPA at 20.0µg/mL.

8.3.2.1.4 Cal Level 4: To a 10mL volumetric flask, add 500µL of Intermediate Initial Calibration Standard (Section 8.3.2) and 500µL of ICAL Surrogate Stock Standard (Section 8.3.1). Bring to volume with Hexane. Final concentration is 0.50µg/mL for all analytes except MCPP and MCPA at 50.0µg/mL.

8.3.2.1.5 Cal Level 5: To a 10mL volumetric flask, add 1.0mL of Intermediate Initial Calibration Standard (Section 8.3.2) and 1mL of ICAL Surrogate Stock Standard (Section 8.3.1). Bring to volume with Hexane. Final concentration is 1.0µg/mL for all analytes except MCPP and MCPA at 100µg/mL.

8.3.2.1.6 Cal Level 6: To a 10mL volumetric flask, add 2.0mL of Intermediate Initial Calibration Standard (Section 8.3.2) and 2mL of ICAL Surrogate Stock Standard (Section 8.3.1). Bring to volume with Hexane. Final concentration is 2.0µg/mL for all analytes except MCPP and MCPA at 200µg/mL.

8.3.2.2 Intermediate Continuing Calibration Standard: To a 10mL volumetric flask, add 1mL of each stock standard listed in Section 8.2.3. Bring to volume with Hexane. Final concentration is 10µg/mL for all analytes except MCPP and MCPA at 1000µg/mL.

8.3.2.2.1 Working Continuing Calibration Standard: To a 20mL volumetric flask, add 400µL of Intermediate Continuing Calibration Standard (Section 8.3.2). Bring to volume with Hexane. Final concentration is 0.2µg/mL for all analytes except MCPP and MCPA at 20µg/mL.

8.4 Internal Standard Solution: 4,4'-dibromooctafluorobiphenyl (DBOB) is used as the internal standard, and is added to all single-component calibration standards and sample extracts to achieve a concentration of 0.25 µg/mL.

8.4.1 Working Internal Standard Solution: To a 10mL volumetric flask, add 1mL of the IS Stock (Section 8.2.1). Bring to volume with Acetone. Final concentration is 25µg/mL. 10µL of this solution is added to the 1mL sample and QC sample extracts to achieve a concentration of 0.25µg/mL for analysis.

8.5 Surrogate Standard: 2,4-Diclorophenylacetic acid (DCAA). The Surrogate standard is added to the calibration standards at the concentrations listed in Table 2, and is spiked into all samples and QC samples prior to extraction.

8.5.1 Working Surrogate Standard Solution: To a 100mL volumetric flask, add 10mL of Surrogate Stock (Section 8.2.4.1). Bring to volume with Acetone. Final concentration is 10µg/mL.

8.6 LCS/MS Spiking Solutions: The LCS/MS spiking solutions are prepared volumetrically by diluting the appropriate free acid stock standards in acetone. The spiking solution concentrations are listed in Table 2.

8.6.1 Working LCS/MS Solution: To a 25mL volumetric flask, add 2.5mL of LCS/MS Stock (Section 8.2.4.2). Bring to volume with Acetone. Final concentration is 10µg/mL for all analytes except MCPP and MCPA at 1000µg/mL.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

A matrix-specific extraction blank is performed with each extraction batch of 20 or fewer samples, according to the extraction SOPs. The extraction blank must not contain any of the reportable analytes at or above the reporting limit. If any reportable analytes are detected in the blank, the entire extraction batch is suspect and re-extraction of all associated samples is required. Appendix 1 contains specific corrective action procedures.

9.2 Laboratory Control Sample (LCS) / LCS Duplicate

A Laboratory Control Sample (LCS) and an LCS Duplicate (LCSD) is extracted with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with all target analytes. The concentrations of the spiking solutions are listed in Table 2. The recovery and RPD acceptance criteria are listed in Table 4. If any recovery criteria are not met, the extract should be reanalyzed. If the criteria are still not met, the entire batch should be re-extracted. If this is not possible, due to insufficient sample or holding time exceedence, the analyst must write up the failure on a narrative sheet for inclusion in the client report. Appendix 1 contains specific corrective action procedures.

9.3 Initial Calibration Verification (ICV)

Prepare calibration standards using the procedures in Section 8.3 and Table 2. The calibration standards are aliquoted into autosampler vials and capped prior to loading onto the autosampler tray. The calibration standards are analyzed and the curve is calculated prior to sample analysis.

9.4 Continuing Calibration Verification (CCV)

A second-source CCV standard must be injected at the beginning of each 12-hour shift prior to conducting any sample analyses. Subsequent continuing calibration standards are injected at intervals of not less than once every twenty samples.

9.5 Matrix Spike (MS)/MS Duplicate

A matrix spike/matrix spike duplicate pair is extracted and analyzed for each batch of 20 or less samples only upon client request. The spike compounds and levels are listed in Table 2. The recovery and RPD acceptance criteria are listed in Table 4. If the recovery criteria are not met, but are met in the LCS, the failure may be attributed to sample matrix effects and must be noted on a narrative sheet for inclusion in the client report. Appendix 1 contains specific corrective action procedures.

9.6 Laboratory Duplicate

Not applicable.

9.7 Method-specific Quality Control Samples

9.7.1 Surrogates

All extracted samples and associated QC are spiked with surrogates at the levels listed in Table 2. The laboratory must evaluate surrogate recovery data from individual samples and QC samples versus the surrogate control limits for both columns listed in Table 3. If the surrogate limits are not met, the extract should be reanalyzed to determine if the failure was due to an instrument problem. If the criteria are still not met, the affected samples should be re-extracted to confirm that the failure was due to sample matrix. If matrix effect is confirmed, this must be noted on a narrative sheet for inclusion in the client report. Appendix 1 contains specific corrective action procedures.

9.8 Method Sequence

Initial calibration:
Instrument Prime
Std Level 1
Std Level 2
Std Level 3
Std Level 4
Std Level 5
Std Level 6
Initial Calibration Verification Standard (ICV)

Daily sequence:

1. Instrument Prime
2. Herbicide Continuing Calibration Standard
3. Extraction Blank
4. Laboratory Control Sample

5. Laboratory Control Sample Duplicate
6. Matrix Spike (Upon Client Request)
7. Duplicate/Matrix Spike Duplicate (Upon Client Request)
8. Samples (typically 4 – 8, however up to 20 may be analyzed)
9. Herbicide Continuing Calibration Standard
10. Repeat 4 – 9 (as needed)

10. Procedure

10.1 Equipment Set-up

10.1.1 Typical Gas Chromatographic Conditions:

Temperature 1:	60 °C	**Detector temperature:**	350 °C
Ramp 1:	9°C/minute	**Carrier gas:**	Helium
Temperature 2:	96°C	**Carrier flow:**	1.7 mL/min
Ramp 2:	21°C/minute	**Carrier mode:**	Constant flow
Temperature 3:	220°C	**Makeup gas:**	Argon/methane (P5)
Ramp 3:	40°C/minute	**Total detector flow:**	55 mL/min
Final Temperature:	280°C	**Injection volume:**	1 µL
Final Time:	15 minutes		
Injector Temperature:	250°C		
Injector Mode:	Spiltless		
Injector Flow:	100mL/min		
Splitless Purge:	On at 0.45 min		
Purge Flow:	95.6 mL/min		

10.2 Initial Calibration

10.2.1 Prepare calibration standards using the procedures in Section 8.3 and Table 2. The calibration standards are aliquoted into autosampler vials and capped prior to loading onto the autosampler tray. The calibration standards are analyzed and the curve is calculated prior to sample analysis.

10.2.2 Calibration Factors

Internal standard calibration techniques are employed in this method.

10.2.2.1 Internal Standard Procedure. In each standard, calculate the response factor (RF) for each analyte, the average RF, and the relative standard deviation (RSD) of the RFs, using the Target data processing software. The calculations are performed automatically, using the formulae listed in Alpha's Quality Manual.

10.2.3 Initial Calibration Criteria

If the RSD for an analyte is $\leq$ 20%, then the response of the instrument for this compound is considered linear over the range and the mean calibration factor (Avg. RF) can be used to quantitate sample results. (Section 9.6.3).

If the RSD for any analyte is > 20%, then linearity through the origin cannot be assumed. The mean response factor cannot be used for quantitation. An alternative calculation may be done by the use of linear regression as long as the correlation coefficient is $\geq$0.99. (The regression equation cannot be forced

through the origin.) The equation for linear regression may be found in Alpha's Quality Manual.

If both of these quantitation methods fail criteria for any compound in the initial calibration, then the system must be reevaluated and a new calibration curve must be analyzed.

10.2.4 Retention Time Windows
The retention time windows used for the identification of target analytes is ± 0.05 minutes. These criteria have been adopted from the EPA CLP Statement of Work (OLM04.2). It has been found that these limits work well, being wide enough to eliminate false-negatives while being tight enough to eliminate false-positives. Windows that are calculated using the procedure recommended in Method 8000 tend to be very narrow, creating the risk of false negative results. The Retention Times are listed in Table 3.

10.2.4.1 The windows listed above are used as guidance, however the experience of the analyst weighs heavily in the interpretation of the chromatograms. For example, it has been observed that certain oil matrices can cause the retention times to shift more dramatically. Additionally, if any positive results are questionable and at a sufficiently high concentration, GC/MS analysis is used for confirmation.

10.2.5 The following compounds often co-elute using the dual column analysis scheme:

- DB-5: 2,4-DB / Dinoseb
- DB-1701: 2,4-D / Pentachlorophenol 2,4-DB / Chloramben

NOTE: 2,4-DB does not co-elute on both channels at the same time.

10.3 Equipment Operation and Sample Processing

10.3.1 The same GC operating conditions used for the initial calibration must be employed for sample analyses, including sample injection volume (Section 9.1.10).

10.3.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the retention time window for the compound. Each tentative identification is confirmed using a second GC column of dissimilar stationary phase. In particularly difficult matrices, confirmation by GC/MS may be advisable (see Section 9.4.9).

10.3.3 The concentration reported for an identified target analyte in an extract is calculated using the Target data processing software. The Target methods have been configured to utilize the quantitation formulas found in Alpha's Quality Manual. Proper quantitation requires the appropriate selection of a baseline from which the peak area or height can be determined. See the Manual Integration SOP for integration guidelines. Also refer to Section 9.6 for calculations.

10.3.3.1 If the responses exceed the calibration range of the system, dilute the extract and reanalyze.

10.3.4 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour analytical shift), or calibration standards interspersed within the samples. When a calibration verification

standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be re-injected.

10.3.5 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. Standards are analyzed after every 4 – 8 samples to minimize the number of samples that must be re-injected should the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

10.3.6 Use the calibration standards analyzed during the sequence to evaluate retention time stability. The retention time windows are established using the absolute retention time of each analyte in the mid-concentration standard during the initial calibration as the mid-point of the window. The widths of the windows are defined in Section 9.2.4.

10.3.7 Each subsequent injection of a standard during the 12-hour analytical shift (i.e., those standards injected every 20 samples, or more frequently) must be checked against the retention time windows. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

10.3.8 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract may be needed. If instrument problems are suspected, rerun the extract on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to the extraction SOPs for the procedures to be followed in sample cleanup.

10.3.9 GC/MS Confirmation

GC/MS confirmation may be used in conjunction with either single-column or dual-column analysis if the concentration is sufficient for detection by GC/MS.

10.3.9.1 Full-scan GC/MS will normally require a concentration of approximately 10ng/µL in the final extract for each single-component compound.

10.3.9.2 The GC/MS must be calibrated for the specific target herbicides when it is used for quantitative analysis.

10.3.9.3 GC/MS may not be used for confirmation when concentrations are below the sensitivity of the instrument.

10.3.9.4 GC/MS confirmation should be accomplished by analyzing the same extract that is used for GC/ECD analysis.

10.3.9.5 The base/neutral/acid extract and the associated blank may be used for GC/MS confirmation if the surrogates and internal standards do not interfere and if it is demonstrated that the analyte is stable during acid/base partitioning. However, if the compounds are not detected in the base/neutral/acid extract, then GC/MS analysis of the pesticide extract should be performed.

10.3.9.6 A QC reference sample containing the compound should also be analyzed by GC/MS. The concentration of the QC reference sample must demonstrate that those pesticides identified by GC/ECD can be confirmed by GC/MS.

10.3.10 If a co-elution pair (Section 9.2.5) exists, the target compounds must be reported from the non-coelution channel.

10.4 Continuing Calibration

10.4.1 A second-source CCV standard must be injected at the beginning of each 12-hour shift prior to conducting any sample analyses. Subsequent continuing calibration standards are injected at intervals of not less than once every 10 samples.

10.4.1.1 The calibration factor (for external standard compounds) and response factor (for internal standard compounds) for each analyte to be quantitated must not exceed a ± 15% difference when compared to the initial calibration curve. The Target data processing software automatically calculates the %D for all analytes according to the formula in Alpha's Quality Manual

If this criterion is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

10.4.1.2 If routine maintenance does not return the instrument performance to meet the QC requirements (Section 10) based on the last initial calibration, then a new initial calibration must be performed. Due to the large number of analytes present, allowances may be made for a CF or RF that drifts out high, as long as there are no positive hits for that particular analyte in any of the associated samples. Any QC failures must be written up by the analyst on narrative sheets for inclusion with the sample data.

10.4.2 Compare the retention time of each analyte in the calibration standard with the absolute retention time windows described in section 9.2.4. The center of the absolute retention time window for each analyte is its retention time in the mid-concentration standard analyzed during the initial calibration. Each analyte in each standard must fall within its respective retention time window. If not, the gas chromatographic system must either be adjusted so that a second analysis of the standard does result in all analytes falling within their retention time windows, or a new initial calibration must be performed and new retention time windows established.

10.4.3 Co-elution pairs (Section 10.2.5) will often separate or come together as the length of the column changes. If a CCV shows a different co-elution pattern than the Initial Calibration, the instrument must be recalibrated for the new pattern(s) and any samples analyzed since the last acceptable calibration verification must be reanalyzed.

10.5 Preventive Maintenance

Routine preventive maintenance should be performed to maintain GC system performance. This includes periodic replacement of injector septa, replacement of injector liner(s), and replacement of injector seals. All maintenance is noted in individual Instrument Maintenance Logbooks.

11. Data Evaluation, Calculations and Reporting

Herbicides are calculated as described in Section 9.4.3, and reported in µg/L or µg/Kg units. After performing technical data review, validating that all QC criteria have been met and confirming all positive hits, the data report is sent electronically to the LIMS computer for generation of the client report. Two levels of review of the data in the LIMS system are preferred prior to release of data. These reviews include analyst review and review by the Department Supervisor or other trained analyst.

11.1 Aqueous Calculation

$$\mu g/L = \frac{(A_s)\,(C_{IS})\,(D)\,(V_f)}{(A_{IS})\,(\overline{RF})\,(V_s)\,(1000)}$$

Where:

A_s = Peak area of analyte
A_{IS} = Peak area of Internal Standard
C_{IS} = Concentration of IS (µg/L)
D = Dilution factor (D = 1 for no dilution)
V_f = Final extract volume (mL)
Vs = Initial volume extracted (mL)

$\overline{RF}$ = Mean response factor

11.2 Soil/Solid Calculation

$$\mu g/Kg = \frac{(A_s)\,(C_{IS})\,(D)\,(V_f)}{(A_{IS})\,(\overline{RF})\,(W_s)\,(1000)}$$

Where:

A_s = Peak area of analyte
A_{IS} = Peak area of Internal Standard
C_{IS} = Concentration of IS (µg/L)
D = Dilution factor (D = 1 for no dilution)
V_f = Final extract volume (mL)
Ws = Initial weight extracted (g)

$\overline{RF}$ = Mean response factor

11.2.1 Response Factor Calculation

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

Where:

A_s = Peak area of analyte
A_{IS} = Peak area of Internal Standard
C_s = Concentration of analyte (µg/L)
C_{IS} = Concentration of IS (µg/L)

11.3 Molecular Weight Correction

In addition, conversion factors for the molecular weights have been listed for all analytes reported under EPA Method 8151.

11.3.1 The calibration is performed using the methyl ester compounds; therefore the calculation of the concentration includes a correction for the molecular weight of the methyl ester versus the acid herbicide.

Derivatized herbicides are used for the standard curve, and they are supplied as

methyl esters as opposed to acid herbicide form which is used for the LCS. The difference between the acid form and the methyl ester is + 14 (i.e. In Derivatization, a -CH_3 group replaces the -H, (15-1 = 14)). The factors used for correction (listed in the Table below) vary for each herbicide and are applied to the standard concentration at each level of the calibration within the target processing software.

Example: 2,4-D

2,4-D MW = 221.04 2,4-D Methyl ester MW = 235.06

If you spike 10 ug of 2,4-D, and derivatized it, you end up with 10.634 ug of 2,4-D Methyl ester that you are measure, as you've stripped the -H and added a -CH3, increasing the molecular weight. The true value for the spike is 10 ug as the acid herbicide, and 10.634 ug as the methyl ester. So a spike of 10 ug of acid, would measure 10.634 ug of the methyl ester to get 100% recovery. The true value for the spike would be 10.634 as methyl ester, which you use to divide your measured value by.

If measuring recoveries, the value of the 10 ug of the methyl ester, would be 10 ug measured (as methyl ester)/10.634 ug spiked (as methyl ester) = 94.04%.

If, on the other hand you want to convert your final result using a correction factor, you would use the MW of the acid/MW of the ester (221.04/235.06 = 0.94).

Conversion Factors:

Parameter	CAS No.[a]	MOL WT.	WT as methyl ester	Conversion Factor
2,4-D [1, 2, 3]	94-75-7	221.04	235.06	0.94
2,4-DB	94-82-6	326.18	340.18	0.96
2,4,5-TP (silvex) [1, 2, 3]	93-72-1	269.51	283.51	0.95
2,4,5-T [1, 2]	93-76-5	255.48	269.48	0.95
Dalapon	75-99-0	142.96	156.96	0.91
Dicamba	1918-00-9	221.04	235.04	0.94
Dichloroprop	120-36-5	235.06	249.06	0.94
Dinoseb	88-85-7	240.21	254.21	0.95
MCPA	94-74-6	200.62	214.62	0.93
MCPP	93-65-2	214.65	228.65	0.94

Parameter	CAS No.[a]	MOL WT.	WT as methyl ester	Conversion Factor
Acifluorfen	50594-66-6	361.66	375.66	0.96
Bentazon	25057-89-0	240.28	254.28	0.94
Chloramben	133-90-4	206.02	220.02	0.93
DCPA diacid[b]	2136-79-0	303.91	317.91	0.95
3,5-Dichlorobenzoic acid	51-36-5	191.01	205.01	0.93
Picloram	1918-02-1	241.46	255.46	0.94
4-Nitrophenol	100-02-1	139.10	153.10	0.91
Pentachlorophenol	87-86-5	266.34	280.34	0.95

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

Refer to Section 10 for specific corrective actions.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Qualtrax Document ID 1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

Qualtrax ID 1732 MDL/LOD/LOQ Generation

Qualtrax ID 1739 IDC/DOC Generation

Qualtrax ID 1728 Waste Management and Disposal SOP

16. Attachments

Table 1: REPORTING LIMITS

Table 2: STANDARD SOLUTIONS

Table 3: RETENTION TIMES OF CHLORINATED HERBICIDES

Table 4: QC ACCEPTANCE CRITERIA

Appendix 1: Table V C-1 Specific QA/QC Requirements and Performance Standards

TABLE 1

REPORTING LIMITS

Herbicides	RL (Aqueous)	RL (Soil)
2,4-D	1.0 ug/L	33 ug/kg
Dalapon	1.0 ug/L	33 ug/kg
2,4-DB	1.0 ug/L	33 ug/kg
Dicamba	1.0 ug/L	33 ug/kg
Dichloroprop	1.0 ug/L	33 ug/kg
Dinoseb	1.0 ug/L	33 ug/kg
MCPA	100.0 ug/L	3300 ug/kg
MCPP	100.0 ug/L	3300 ug/kg
Silvex (2,4,5-TP)	1.0 ug/L	33 ug/kg
2,4,5-T	1.0 ug/L	33 ug/kg

TABLE 2

STANDARD SOLUTIONS

Compound	Level 6	Level 5	Level 4	Level 3	Level 2	Level 1	Std. Spike Concentration *	Std. LCS Concentration *
	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)	(µg/mL)
2,4-D	2.0	1.0	0.5	0.2	0.1	0.05	10	10
Dalapon	2.0	1.0	0.5	0.2	0.1	0.05	10	10
2,4-DB	2.0	1.0	0.5	0.2	0.1	0.05	10	10
Dicamba	2.0	1.0	0.5	0.2	0.1	0.05	10	10
Dicloroprop	2.0	1.0	0.5	0.2	0.1	0.05	10	10
Dinoseb	2.0	1.0	0.5	0.2	0.1	0.05	10	10
MCPA	200	100	50	20	10	5	1000	1000
MCPP	200	100	50	20	10	5	1000	1000
Silvex (2,4,5-TP)	2.0	1.0	0.5	0.2	0.1	0.05	10	10
2,4,5-T	2.0	1.0	0.5	0.2	0.1	0.05	10	10
3,5-Dichlorobenzoic Acid	2.0	1.0	0.5	0.2	0.1	0.05	10	10
4-Nitrophenol	2.0	1.0	0.5	0.2	0.1	0.05	10	10
Chloramben	2.0	1.0	0.5	0.2	0.1	0.05	10	10
Pentachlorophenol	2.0	1.0	0.5	0.2	0.1	0.05	10	10
Bentazon	2.0	1.0	0.5	0.2	0.1	0.05	10	10
Picloram	2.0	1.0	0.5	0.2	0.1	0.05	10	10
DCPA Diacid	2.0	1.0	0.5	0.2	0.1	0.05	10	10
Acifluorfen	2.0	1.0	0.5	0.2	0.1	0.05	10	10
DCAA (Surrogate)	2.0	1.0	0.5	0.2	0.1	0.05	10	10

***** Calculations are based on an initial aqueous sample volume of 1L**,** initial soil sample weight of 30g, and final extract volume of 10mL.

TABLE 3

Typical RETENTION TIMES (minutes) of METHYL DERIVATIVES of CHLORINATED HERBICIDES

ANALYTE	Narrow-Bore Columns	
	Primary Column	Confirmation Column
Dalapon	3.9	4.0
3,5-Dichlorobenzoic Acid	15.9	16.0
4-Nitrophenol	18.3	16.12
DCAA (surrogate)	19.4	18.8
Dicamba	19.9	19.1
Dichloroprop	22.2	21.3
2,4-D	23.2	21.8
DBOB (internal standard)	22.8	22.9
Pentachlorophenol	23.3	23.6
Chloramben	27.2	24.5
2,4,5-TP	25.1	24.4
2,4,5-T	26.2	25.0
2,4-DB	27.2	26.3
Dinoseb	28.6	26.4
Bentazon	29.1	27.0
Picloram	31.2	28.0
DCPA diacid[a]	29.8	29.1
Acifluorfen	35.6	33.4
MCPP	20.5	19.9
MCPA	21.3	20.3

Primary Column: **DB-5:** 30m x 0.32mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, SPB-5, RTx-5 , or equivalent), 0.25µm film thickness.

Confirmation Column: **DB-1701:** 30m x 0.32mm ID fused silica capillary column chemically bonded with 50 percent phenyl methylpolysiloxane (DB-1701, or equivalent) 0.25µm film thickness.

Temperature Program: See Section 10.1

Helium Carrier Flow: 1.7mL/min

Injection Volume: 1µL, splitless, 45 sec delay

Injector Temperature: 250ºC

Detector Temperature: 320ºC

[a] DCPA monoacid and diacid metabolites included in method scope; DCPA diacid metabolite used for validation studies. DCPA is a dimethyl ester.

TABLE 4
QC ACCEPTANCE CRITERIA

	Aqueous		Soil	
Surrogate % Recovery	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**
2,4-Diclorophenylacetic acid (DCAA)	30%	150%	30%	150%

	Aqueous % Recovery		Soil % Recovery	
LCS	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**
2,4-D	30%	150%	30%	150%
dalapon	30%	150%	30%	150%
2,4-DB	30%	150%	30%	150%
dicamba	30%	150%	30%	150%
dicloroprop	30%	150%	30%	150%
dinoseb	30%	150%	30%	150%
MCPA	30%	150%	30%	150%
MCPP	30%	150%	30%	150%
Silvex (2,4,5-TP)	30%	150%	30%	150%
2,4,5-T	30%	150%	30%	150%

MCP only	**Aqueous % Recovery**		**Soil % Recovery**		**% RPD**	
LCSD	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**	**Aqueous**	**Soil**
2,4-D	40%	140%	40%	140%	≤ 25%	≤ 25%
dalapon	40%	140%	40%	140%	≤ 25%	≤ 25%
2,4-DB	40%	140%	40%	140%	≤ 25%	≤ 25%
dicamba	40%	140%	40%	140%	≤ 25%	≤ 25%
dicloroprop	40%	140%	40%	140%	≤ 25%	≤ 25%
dinoseb	40%	140%	40%	140%	≤ 25%	≤ 25%
MCPA	40%	140%	40%	140%	≤ 25%	≤ 25%
MCPP	40%	140%	40%	140%	≤ 25%	≤ 25%
Silvex (2,4,5-TP)	40%	140%	40%	140%	≤ 25%	≤ 25%
2,4,5-T	40%	140%	40%	140%	≤ 25%	≤ 25%

	Aqueous % Recovery		Soil % Recovery		Duplicate and/or MSD	
MS / MSD	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**	**Aqueous RPD**	**Soil RPD**
2,4-D	30%	150%	30%	150%	30%	30%
dalapon	30%	150%	30%	150%	30%	30%
2,4-DB	30%	150%	30%	150%	30%	30%
dicamba	30%	150%	30%	150%	30%	30%
dicloroprop	30%	150%	30%	150%	30%	30%
dinoseb	30%	150%	30%	150%	30%	30%
MCPA	30%	150%	30%	150%	30%	30%
MCPP	30%	150%	30%	150%	30%	30%
Silvex (2,4,5-TP)	30%	150%	30%	150%	30%	30%
2,4,5-T	30%	150%	30%	150%	30%	30%

Appendix 1: Table V C-1 Specific QA/QC Requirements and Performance Standards

Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup	BWSC-CAM	Table V C-1
Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 8151A, Chlorinated Herbicides by Gas Chromatography	28 May 2004	Revision No. 2
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Title: **Specific QA/QC Requirements and Performance Standards for SW-846 Method 8151A**

Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Retention Time Windows	Laboratory Analytical Accuracy	(1) Prior to initial calibration and when a new GC column is installed. (2) Calculated according to the method. (Section 7.6 of SW-846 8000).	No	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) Minimum of 5 standards. (2) Low standard must be ≤ reporting limit. (3) %RSD should be ≤20 or "r" should be ≥0.99. (4) If regression analysis is used, the curve must not be forced through the origin. (5) Curves must be verified by an independent ICV before analysis. (6) All standards must be derivitized using the same procedures used for samples, whether prepared in the laboratory or purchased from a vendor.	No	Recalibrate as required by method.	Report exceedances in case narrative.
Continuing Calibration (CCAL)	Laboratory Analytical Accuracy	(1) Prior to samples, every 12 hours or every 10 samples, whichever is more frequent, and at the end of the analytical sequence. (2) Concentration level near midpoint of curve. (3) Percent difference or percent drift of calibration factors should be ≤15. (4) Verify all analytes fall within retention time windows. (5) All standards must be derivitized using the same procedures used for samples, whether prepared in the laboratory or purchased from a vendor.	No	(1) Perform instrument maintenance, reanalyze CCAL and/or recalibrate as required by method. (2) Reanalyze "associated samples" if beginning or closing CCAL exhibited low response and associated herbicides were or were not detected in samples. (3) Reanalyze "associated samples" if beginning or closing CCAL exhibited high response and associated herbicides were detected in the samples. NOTE: "Associated Samples" refers to all samples analyzed since the last acceptable CCAL.	Report exceedances in case narrative.
Method Blanks	Laboratory Method Sensitivity (contamination evaluation)	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Matrix-specific (e.g., water, soil). (3) Target analytes must be less than or equal to reporting limit.	Yes	Locate source of contamination; correct problem; re-extract associated samples if contaminants are present in the method blank.	(1) Report nonconformances in case narrative. (2) If contamination of method blanks is suspected or present, the laboratory, using a "B" flag or some other convention (such as the case narrative), should qualify the sample results. (3) If re-extraction is performed within holding time, the laboratory may report results of the re-extraction only. (4) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction.

Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup

Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 8151A, Chlorinated Herbicides by Gas Chromatography

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Title: **Specific QA/QC Requirements and Performance Standards for SW-846 Method 8151A**

Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Laboratory Control Spikes (LCSs)	Laboratory Method Accuracy	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Prepared using standard source different than used for initial calibration. (3) Concentration level should be ≤ mid-level standard. (4) Must contain all target analytes. (5) Matrix-specific (e.g., soil, water). (6) Percent recoveries must be between 40-140. (7) Laboratories are expected to develop their own in-house control limits, which should fall within the limits listed above.	Yes	Recalculate the percent recoveries. Check MS/MSD; if recoveries are acceptable in MS/MSD, nonconformance may be isolated to LCS. If recoveries are outside criteria in MS/MSD, re-extract associated samples.	(1) Report exceedances in case narrative. (2) If re-extraction is performed within holding time, the laboratory may report results of the re-extraction only. (3) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction.
LCS Duplicate	Laboratory Method Precision	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Prepared using same standard source and concentration as LCS. (3) Must contain all target analytes. (4) Analyze immediately after LCS. (5) Laboratory-determined percent recoveries must be between 70 – 130 for target compounds (6) Matrix-specific (e.g., soil, water); and (7) Laboratory-determined Relative Percent Difference (RPD) must be ≤ 25.	Yes	Recalculate RPD; Locate source of problem; Narrate non-conformances	(1) Locate and rectify source of non-conformance before proceeding with the analyses of subsequent sample batches. (2) Narrate non-conformances
MS/MSDs	Method Accuracy in Sample Matrix Method Precision in Sample Matrix	(1) Extracted with every 20 samples (BATCH QC). (2) Matrix-specific. (3) Prepared using standard source different than that used for initial calibration. (4) Concentration level should be between low and mid-level standard. (5) Must contain all target analytes. (6) Percent recoveries should be between 30-150. (7) RPDs should be ≤30 for single-component analytes and ≤50 for multi-component analytes.	Yes (Only when requested by the data-user)	Check LCS; if recoveries acceptable in LCS, evaluate potential cleanup techniques (Section 7.2.4 of SW-846 8151A) for samples associated with MS/MSD.	Report exceedances in case narrative.

Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup

Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 8151A, Chlorinated Herbicides by Gas Chromatography

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Title: **Specific QA/QC Requirements and Performance Standards for SW-846 Method 8151A**

Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Surrogates	Accuracy in Sample Matrix	(1) Minimum of 1, that encompasses range of temperature program used in method and does not interfere with the target analytes. Recommended surrogate: DCAA (2) Percent recoveries must be between 30-150 for surrogate on both columns. (3) Laboratories are expected to develop their own in-house control limits, which should fall within the limits listed above. (4) If the surrogate exceeds limits on one column and greater than RL concentrations on both columns are not comparable (RPD > 40), re-extract and re-analyze the sample	Yes (report surrogate recoveries from both columns)	(1) If the surrogate is outside limits on both columns, re-extract and re-analyze the sample. (2) If a surrogate is diluted to a concentration below that of the lowest calibration standard, no corrective action is necessary. (3) If the surrogate exceeds limits on one column only, and the results on both columns are below RLs, no corrective action is necessary. (4) If the surrogate exceeds limits on one column only, and results on both columns are comparable (RPD < 40), then no corrective action is necessary.	(1) Report exceedances in case narrative. (2) If re-extraction or reanalysis yields similar surrogate nonconformances, the laboratory should report results of both extractions or analyses. (3) If re-extraction or reanalysis is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the re-extraction or reanalysis only. (4) If re-extraction or reanalysis is performed outside of holding time and yields acceptable surrogate recoveries, the laboratory must report results of both the initial and re-extraction or reanalysis. (5) If sample is not re-extracted or reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.
Internal Standards *(Optional)*	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	(1) Minimum of 1. Recommended Internal Standard: DBOB (2) Area counts in samples must be between 50 – 200% of the area counts in the associated continuing calibration standard. (3) Retention times of internal standards must be within calculated retention time windows.	No	If internal standard is outside limits, reanalyze sample unless obvious interference present.	(1) Report exceedances in case narrative. (2) If reanalysis yields similar internal standard nonconformance, the laboratory should report both results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable internal standard recovery, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time and yields acceptable internal standard recovery, the laboratory must report results of both analyses. (5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.

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Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 8151A, Chlorinated Herbicides by Gas Chromatography	28 May 2004	Revision No. 2
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Title: **Specific QA/QC Requirements and Performance Standards for SW-846 Method 8151A**

Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Identification and Quantitation	Inter-laboratory consistency	(1) Laboratory should use the average calibration factor of each analyte for quantitation. (2) Secondary column analysis: Laboratory must utilize a second dissimilar column to confirm positive herbicide results. The laboratory must report the higher of the two results unless obvious interference is present on one of the columns in which case the laboratory can report the lower result. All required QA/QC parameters (e.g., calibrations, LCSs, etc.) must be met on the secondary column as well. (3) If calibration standards are prepared using methyl esters, the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.	No	NA	If the RPD between the dual column results exceeds 40, the laboratory should qualify the sample results and/or note the exceedance in the case narrative. NOTE: If the high RPD can be definitively attributed to interference on one of the two columns, the laboratory should report the lower value and provide a discussion in the case narrative that this approach was employed.
General Reporting Issues	NA	(1) The laboratory must report values ≥ the sample-specific reporting limit; optionally, values below the sample-specific reporting limit can be reported as estimated, if requested. The laboratory must report results for samples and blanks in a consistent manner. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported.	Yes	NA	(1) Qualification of the data is required if reporting values below the sample-specific reporting limit. (2) Recommendation is that the reporting of diluted and undiluted analyses should be a must to be consistent with the inorganic reporting convention of reporting all dilutions and to ensure the lowest possible reporting limit can be achieved if the data is available.

GC = Gas Chromatography
MS/MSDs = Matrix Spikes/Matrix Spike Duplicates
%RSD = Percent Relative Standard Deviation
DCAA = 2,4-Dichlorophenylacetic Acid

"r" = Correlation Coefficient
RPDs = Relative Percent Differences
ICV = Initial Calibration Verification – separate source standard
DBOB = 4,4'-Dibromooctafluorobiphenyl

Mercury in Liquid Waste

(Automated Cold-Vapor Technique)

Reference Method No.: **EPA 7470A**

Reference: SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update II, September 1994.

1. Scope and Application

Matrices: Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

Definitions: See Alpha Laboratories Quality Manual Appendix A.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the Mercury Analyzer and in the interpretation of Mercury data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.1 Method Modifications from Reference

2.1.1 A smaller sample sized is prepared, and therefore proportionately less reagent volumes are used.

2.1.2 The original method does not address the automated instrument procedure.

3. Reporting Limits

The typical reporting limit for Mercury is 0.0002mg/L. This satisfies Massachusetts, GW1 and GW 2 criteria. Connecticut mobility criteria for SPLP is 0.0004mg/L, Rhode Island is 0.002mg/L, and the Drinking Water reporting limit is 0.0002mg/L.

4. Interferences

Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analysis is conducted under a laboratory exhaust hood. The analyst must wear chemical resistant gloves when handling concentrated mercury standards.

The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Therefore, the acidification of samples is to be conducted under a laboratory exhaust hood.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in either glass or plastic containers.

6.2 Sample Preservation

Samples are preserved with HNO_3 to a pH of <2.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples are stored under refrigeration at 4 ± 2°C and analyzed as soon as possible after collection. The samples have a 28-day holding time from the time of collection.

7. Equipment and Supplies

Instrumentation:

Perkin Elmer FIMS 100 Atomic absorption spectrophotometer: Use instrument settings recommended by the manufacturer. The PE FIMS is designed specifically for the measurement of mercury using the cold-vapor technique with BOC (background offset correction) performed by a survey scan prior to each sample introduction. PE S10 autosampler is coupled to the instrument.

Cetac M-6100 Atomic absorption spectrophotometer: Use instrument settings recommended by the manufacturer. This instrument employs a reference cell off-set correction and full automation through the CETAC software. A Cetac ASX-260 autosampler is coupled to the instrument.

7.1 Graduated cylinder: Rinse once with 50% HNO_3 and then rinse with reagent water prior to use.

7.2 Volumetric Flasks, Class A, various volumes: Rinse once with 50% HNO_3 and then rinse with reagent water prior to use.

7.3 Heating Block: Environmental Express HotBlock, 48 position capacity, able to maintain 95˚C +/-3.

7.4 50 mL Digestion Tubes: Polypropylene, graduated.

7.5 50 mL Digestion Tube Rack: 48 position, racklock

7.6 Pump tubing: Environmental Express, three stop and two in various IDs.

7.7 PTFE membranes: Whatman TE37 disks.

7.8 Dilution vials: 20mL capacity, used to prepare analytical dilutions.

7.9 Low Dust Laboratory Wipes

7.10 Compressed Air

7.11 Whatman 41 filter paper or equivalent

8. Reagents and Standards

8.1 Reagent Water: Reagent water is DI water shown to be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

8.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade. Store at room temperature in an appropriately designated acid cabinet.

8.3 Hydrochloric acid, concentrated: Trace Metal grade. Store at room temperature in an appropriately designated acid cabinet.

8.4 Carrier, Hydrochloric Acid, 3%: This is the ***carrier*** for the Instrument. In a 1L volumetric flask, add 30mL concentrated trace grade HCl (Section 8.3). Bring to volume with reagent water. Store at room temperature, prepare daily as needed.

8.5 Reductant, Stannous Chloride in 3% HCl: This is the ***reductant*** for the Instrument. In a 1L volumetric flask, add 30mL concentrated trace grade HCl and 11g $SnCl_2 \cdot 2H_20$. Mix to dissolve the solid and bring to volume with reagent water. Store at room temperature, prepare daily as needed.

8.6 Nitric acid (HNO_3), concentrated: Trace metal grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid. Store at room temperature in an appropriately designated acid cabinet.

8.7 Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride in reagent water and dilute to 100mL. Store at room temperature. Expires one month from date of preparation.

8.8 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water. Store at room temperature. Expires one month from date of preparation.

8.9 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of reagent water. Store at room temperature. Expires one month from date of preparation.

8.10 Mercury Stock Standard, 1000ppm: Purchased from a commercial source with a certificate of analysis. Purchase three different sources. Store at room temperature. Expires upon manufacturer's specification.

8.11 Mercury Stock Calibration Standard, 10ppm: To a 100mL volumetric flask, add 5mL of concentrated HNO_3, 2.5mL of concentrated H_2SO_4 and 1000ppm Mercury Stock Standard (Section 8.10, use one source). Bring to volume with reagent water. Store at room temperature. Expires one month from date of preparation.

8.12 Mercury Working Calibration Standard / Matrix Spike Solution, 0.1ppm: To a 100mL volumetric flask, add 5mL of concentrated HNO_3, 2.5mL of concentrated H_2SO_4 and 1mL of 10ppm Mercury Stock Standard (Section 8.11). Bring to volume with reagent water. Store at room temperature. Make fresh daily.

8.13 Mercury Calibration Standards: All calibration standards are prepared daily.

8.13.1 0 ppm Calibration Standard: Add 10 mL of reagent water to a polypropylene digestion vessel. This aliquot may be used for the CCB. Another separate aliquot is prepared in the same manner for use as the ICB and diluent for sample dilutions.

8.13.2 0.0002ppm Calibration Standard: Add 10 mL of reagent water to a polypropylene digestion vessel. Pipet 0.05 mL of 0.1ppm Mercury Working Stock (Section 8.12) to the digestion vessel. Bring to a final volume of 25 mL.

8.13.3 0.001ppm Calibration Standard: Add 10 mL of reagent water to a polypropylene digestion vessel. Pipet 0.25 mL of 0.1ppm Mercury Working Stock (Section 8.12) to the digestion vessel. Bring to a final volume of 25 mL.

8.13.4 0.002ppm Calibration Standard Add 10 mL of reagent water to a polypropylene digestion vessel. Pipet 0.5 mL of 0.1ppm Mercury Working

Stock (Section 8.12) to the digestion vessel. Bring to a final volume of 25 mL.

8.13.5 **0.005ppm Calibration Standard/Continuing Calibration Verification Standard:** Add 10 mL of reagent water to a polypropylene digestion vessel. Pipet 1.25 mL of 0.1ppm Mercury Working Stock (Section 8.12) to the digestion vessel. Bring to a final volume of 25 mL.

8.13.6 **0.010ppm Calibration Standard / Post Analytical Spike Solution:** Add 10 mL of reagent water to a polypropylene digestion vessel. Pipet 2.5 mL of 0.1ppm Mercury Working Stock (Section 8.12) to the digestion vessel. Bring to a final volume of 25 mL.

8.13.7 **0.020ppm Calibration Standard / Post Analytical Spike Solution:** Add 10 mL of reagent water to a polypropylene digestion vessel. Pipet 5.0 mL of 0.1ppm Mercury Working Stock (Section 8.12) to the digestion vessel. Bring to a final volume of 25 mL.

8.14 Mercury Stock LCS Standard, 10ppm: To a 100mL volumetric flask add 25mL of reagent water and 5mL of concentrated HNO_3 (Section 8.6). Add 1mL of 1000ppm Mercury Stock Standard (Section 8.10). Bring to volume with reagent water. Store at room temperature. Expires one month from date of preparation.

8.15 Mercury Working LCS Standard, 0.1ppm: To a 100mL volumetric flask add 25mL of reagent water and 5mL concentrated HNO_3 (Section 8.6). Add 1mL of 10ppm Stock LCS Standard (Section 8.14). Bring to volume with reagent water. Store at room temperature. Expires one week from date of preparation.

8.16 Mercury LCS Standard, 0.001ppm: Prepare daily with each batch of samples. To a 50mL digestion vessel add 10mL of reagent water Add 0.25 mL of 0.1ppm Working LCS Standard (Section 8.15). Bring to a final volume of 25mL and carry through entire digestion process as in Section 10.1.1.

8.17 Mercury Stock ICV Standard, 10ppm: To a 100mL volumetric flask add 25mL of reagent water and 5mL of concentrated HNO_3 (Section 8.6). Add 1mL of 1000ppm Mercury Stock Standard (Section 8.10-use alternate source than that used for both the calibration standards and the LCS Stock Standard). Bring to volume with reagent water. Store at room temperature. Expires one month from date of preparation.

8.18 Mercury Working ICV Standard, 0.3ppm: To a 100mL volumetric flask add 25mL of reagent water and 5mL of concentrated HNO_3 (Section 8.6). Add 3mL of 10ppm Stock ICV Standard (Section 8.5). Bring to volume with reagent water. Store at room temperature. Expires one week from date of preparation.

8.19 Mercury ICV Standard, 0.003ppm: Prepare daily with each batch of samples. To a 25mL digestion vessel add 10mL of reagent water. Add 0.25mL of 0.3ppm Working ICV Standard (Section 8.18). Bring to a 25mL final volume with reagent water and carry through entire digestion process as in Section 10.1.1..

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

The ICB, CCB, and Method Blank: A 25mL aliquot of 0ppm calibration standard brought through the preparation procedure as outlined in Section 10.1.1 . Blank results must be <RL. See Section 12.1 for corrective action. An ICB is analyzed after the initial calibration or re-calibration. The CCB is analyzed at every 10 sample injection interval. Method Blank is analyzed once per batch of samples; batch consists of 20 samples.

9.2 Laboratory Control Samples (LCS)

The LCS Standard consists of a 0.001ppm Mercury LCS Standard (Section 8.16). This standard is brought through the preparation procedure as outlined in Section 10.1.1. The LCS Standard must be recovered within ± 20% of the true value. See Section 12.3 for corrective action. The LCS Standard is analyzed once per batch of samples. A batch consists of 20 samples.

9.3 Initial Calibration verification (ICV)

The ICV Standard consists of a 25mL aliquot of 0.003ppm Mercury ICV Standard (Section 8.19). The ICV must be recovered within 10% of the true value. See Section 12.2 for corrective action.

9.4 Continuing Calibration Verification (CCV)

The CCV Standard consists of a 0.010ppm calibration standard (Section 8.13.3). The CCV must be recovered within 20% of the true value. See Section 12.2 for corrective action.

9.5 Matrix Spike

A matrix spike is analyzed once per batch of samples. A batch consists of 20 samples for monitoring wells, surface waters, influents and effluents. Prepare the matrix spike at 0.005ppm by adding 1.25mL of 0.1ppm Mercury Stock Standard (Section 8.3) to 25mL of the selected QC sample. The final concentration of the matrix spike is 0.005mg/L.

The matrix spike sample is brought through the preparation procedure as outlined in Section 10.1. A matrix spike is analyzed once per batch of samples. A batch consists of 20 samples for monitoring wells and surface waters. The recovery of the matrix spike must be between 75 – 125% (using the calculation in Section 11.2).

If the recovery of the matrix spike is out of range, a post-analytical spike is analyzed. Prepare the post analytical spike by adding 5mL of 0.010ppm Calibration Standard / Post Analytical Spike Solution (Section 8.1.6) and 5mL of the sample digestate to a 50mL centrifuge tube for a final concentration of 0.005mg/L. Analyze the post spike as outlined in Section 10.3.5.

Calculate the post spike concentration as follows:

Post Analytical Spike Sample Concentration (mg/L) =

[Sample Concentration (mg/L) x (0.5)] + 0.005mg/L

The percent recovery of the post-analytical spike must be between 75 – 125%. See Section 12.4 for corrective action.

9.6 Laboratory Duplicate

A sample is analyzed in duplicate once per batch of samples. A batch consists of 20 samples for monitoring wells and surface waters. The RPD between the sample and its duplicate must be 20% or less (using the calculation in Section 11.3), See Section 12.5 for corrective action.

9.7 Method-specific Quality Control Samples

Not applicable.

9.8 Method Sequence

- Calibration Blank
- 0.0002 ppm Calibration Standard
- 0.0005 ppm Calibration Standard
- 0.001 ppm Calibration Standard
- 0.002 ppm Calibration Standard
- 0.010 ppm Calibration Standard
- 0.020 ppm Calibration Standard
- ICV
- ICB
- Ten analytical samples
- CCV
- CCB
- Ten analytical samples
- CCV
- CCB
- Etc.

10. Procedure

10.1 Equipment Set-up

10.1.1 Preparation and Digestion

Samples, Standards and All Batch QC

Transfer 25mL of well-homogenized sample (or an aliquot of the sample diluted to 25mL with reagent water) or standards (Sections 8.13.1 through 8.13.7, 8.16 and 8.19) to a 50mL centrifuge tube.

Add 1.25mL of concentrated H_2SO_4 (Section 8.2), 0.625mL of concentrated HNO_3 (Section 8.6), Add 3.75mL of Potassium Permanganate Solution, shake and add additional portions of potassium permanganate solution (if necessary) to all samples and QC, until the purple color persists for at least 15 min. (Section 8.8). Add 2mL of Potassium Persulfate Solution (Section 8.9), and heat samples for 2 hours in a 95°C +/-3 heating block. Cool, and add 1.5mL of Sodium Chloride-Hydroxylamine hydrochloride solution (Section 8.7).
Filter the sample if needed to remove any sediment or particulate.

Analyze samples and the digested calibration standards (Sections 8.13.1 through 8.13.7) are used in Section 9.2 to generate a calibration curve.

10.2 Initial Calibration

Construct a calibration curve by plotting the absorbances of prepared standards (Section 10.1.1) versus micrograms of mercury. Determine the peak height of the unknown from the absorbance maxima on the spectrometer, and read the mercury value from the standard curve. (See Section 11.)

The curve correlation coefficient (cc) must be greater than or equal to 0.995 in order for the curve to be linear. If the correlation coefficient is less than 0.995, find and correct the problem. When the problem has been corrected, re-analyze either the previous standards or new standards. When the curve has generated an acceptable cc then the analysis can continue with the ICV/ICB.

10.3 Equipment Operation and Sample Processing

Sample and standard analysis:

10.3.1 Instrument Setup

10.3.1.1 Turn the instrument on. The autosampler will initialize itself.

10.3.1.2 Choose the instrument software from the desktop menu. The autosampler will initialize again.

FIMS 100 NOTE: The instrument must be turned on before the application is started. Otherwise, an error message will result.

10.3.1.3 Enter the appropriate fields for sample identification, and data storage.

10.3.1.4 Fill the carrier and reductant bottles.

10.3.1.4.1 The Carrier is 3% HCl (Section 8.6).

10.3.1.4.2 The Reductant is 1.1% $SnCl_2$ in 3% HCl (Section 8.5).

10.3.1.5 Allow the instrument to warm up while clearing samples. Samples that are cloudy or with particulate present after clearing must be filtered through Whatman 41 filter paper (Section 7.11) before analysis.

10.3.1.6 Place carrier uptake line and reductant uptake line.

10.3.1.7 Load carrier and reductant lines into pump magazines

10.3.1.8 Load the two waste lines into the pump magazines below the roller.

10.3.1.9 Lock the magazines into place.

FIMS100 only:

10.3.1.10 Remove the cap from the liquid/vapor separator and wipe dry with a Lab Wipe (Section 7.9). Compressed air (Section 7.10) through the vapor transfer line to dry it out.

10.3.1.11 Place a PTFE membrane (Section 7.7), rough side up, in the liquid/vapor separator; replace the cap and reattach the vapor transfer line to the sample absorption cell.

10.3.1.12 Adjust the gas flow by turning the black knob below the air flow meter to obtain a reading of just over 50.

10.3.2 Calibration and Sample Analysis

10.3.2.1 The instrument will now run the calibration standards; verify a CC of 0.995 or better before proceeding with the ICV and ICB. Ten analytical samples, a CCV and CCB, ten analytical samples, CCV, CCB, etc. The CCBs and CCVs must be recovered within the proper ranges (Sections 9.4 and 9.1.3) for analysis to continue.

10.3.2.2 If the sample result is beyond 90% of the concentration of the highest point on the calibration curve or LDR study used to establish the linear range, dilute the sample extract with a portion of one of the prepared blanks (ICB, CCB or PBS) to produce an analytical result that is within the range.

10.3.3 Instrument Shut Down

10.3.3.1 When analysis is complete place reagent uptake lines in a beaker of reagent water.

10.3.3.1.1 Continue to run the pumps for several minutes to flush reagents out of the lines.

10.3.3.1.2 Continue to run the pumps for several minutes to flush reagents out of the lines.

10.3.3.2 Pull the reagent uptake lines out of the reagent water beaker to allow the pump to draw air through the lines.

10.3.3.3 Unlock the top and bottom pump magazines and remove tubing from the magazines.

10.3.3.4 Exit from the software application.

10.3.3.4.1 Dump the samples and instrument waste in the Metals/WetChem waste drum located in the transfer room.

10.4 Continuing Calibration

Continuing calibration verification samples are analyzed after every 10 samples in the sample run, as outlined in Section 10.3.5.

10.5 Preventative Maintenance

Preventative maintenance is conducted per the manufacturer's instructions. All preventative maintenance is recorded in the Instrument Maintenance Logbook.

11. Data Evaluation, Calculations and Reporting

11.1 Calculate Mercury concentration

Calculate Mercury concentration from the daily calibration curve. The curve is generated utilizing a straight-line equation defined as:

$$A = k_1 + k_2C$$

Where:

A = Average peak height of the sample/standard integrations
C = Sample/Standard Concentration, µg/L
k_1 = y-intercept
k2 = slope

The instrument will plot peak height against concentration (µg/L). The result is generated in µg/L . This value is divided by 1000 to convert the units to mg/L. If the sample is diluted (DF), the result is multiplied by the DF to generate the final result.

Result, mg/L = (concentration, µg/L) x (1mg/1000µg) x (DF)

11.2 Matrix Spike Calculation

Calculate percent recovery for the Matrix Spike corrected for concentrations measured in the unfortified sample. Percent recovery is calculated using the following equation:

$$\% \text{ Recovery} = \frac{(Cm - C)}{s} \times 100$$

Where:

Cm = measured Mercury in the fortified sample
C = measured native mercury sample concentration
S = concentration equivalent of spike added to sample

11.3 Relative Percent Difference (RPD) Calculation

Calculate the Relative Percent Difference (RPD) for each Duplicate of the initial quantitated concentration (IC) and duplicate quantitated concentration (Dc) using the following formula:

$$RPD = \frac{|(IC - Dc)|}{\{(IC + Dc) / 2\}} \times 100$$

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

12.1 Method Blank Failure: When a prep blank mercury level constitutes 10% or more of analyte level determined for any sample in the batch, or is greater than 2.2x the MDL value (whichever is greater), the associated samples in the batch must be redigested (Section 10.1).

For method blanks that have concentrations greater than the RL, the data is rejected and the associated samples sent back for redigestion unless the associated sample concentrations are greater than 10x the blank concentration. In this case the blank is narrated and the results are reported without qualification.

12.2 ICV / CCV Failure: If the ICV %Recovery is outside of acceptance criteria, the ICV is reinjected. If the %Recovery is outside the acceptance criteria, the analysis is terminated until the problem is found and corrected. If the CCV %Recovery is outside of acceptance criteria, the CCV is reinjected. If the % Recovery is still outside the acceptance criteria, all samples analyzed since the last acceptable CCV must be reanalyzed following correction of the problem.

12.3 LCS Failure: If the LCS is not recovered within acceptance criteria, the LCS is reinjected. If the % Recovery is still outside the acceptance criteria, either recalibrate and rerun or the associated batch and another LCS must be redigested (Section 10.1).

12.4 Matrix Spike / Post Digestion Spike Failure: If the recovery of the matrix spike is outside of the acceptance criteria, a post digestion spike is performed (Section 9.54). If the post digestion spike is outside of 75 – 125%, a narrative must be included with the data. (Section 10.1).

12.5 Duplicate Failure: If the RPD between the sample and its duplicate is greater than 20%, visually evaluate the sample matrix. If the matrix appears problematic, the sample digestate may be diluted and reanalyzed, or a narrative included with the data to explain the matrix problem.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP 1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP 1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/1732 DL/LOD/LOQ Generation

SOP/1739 IDC/DOC Generation

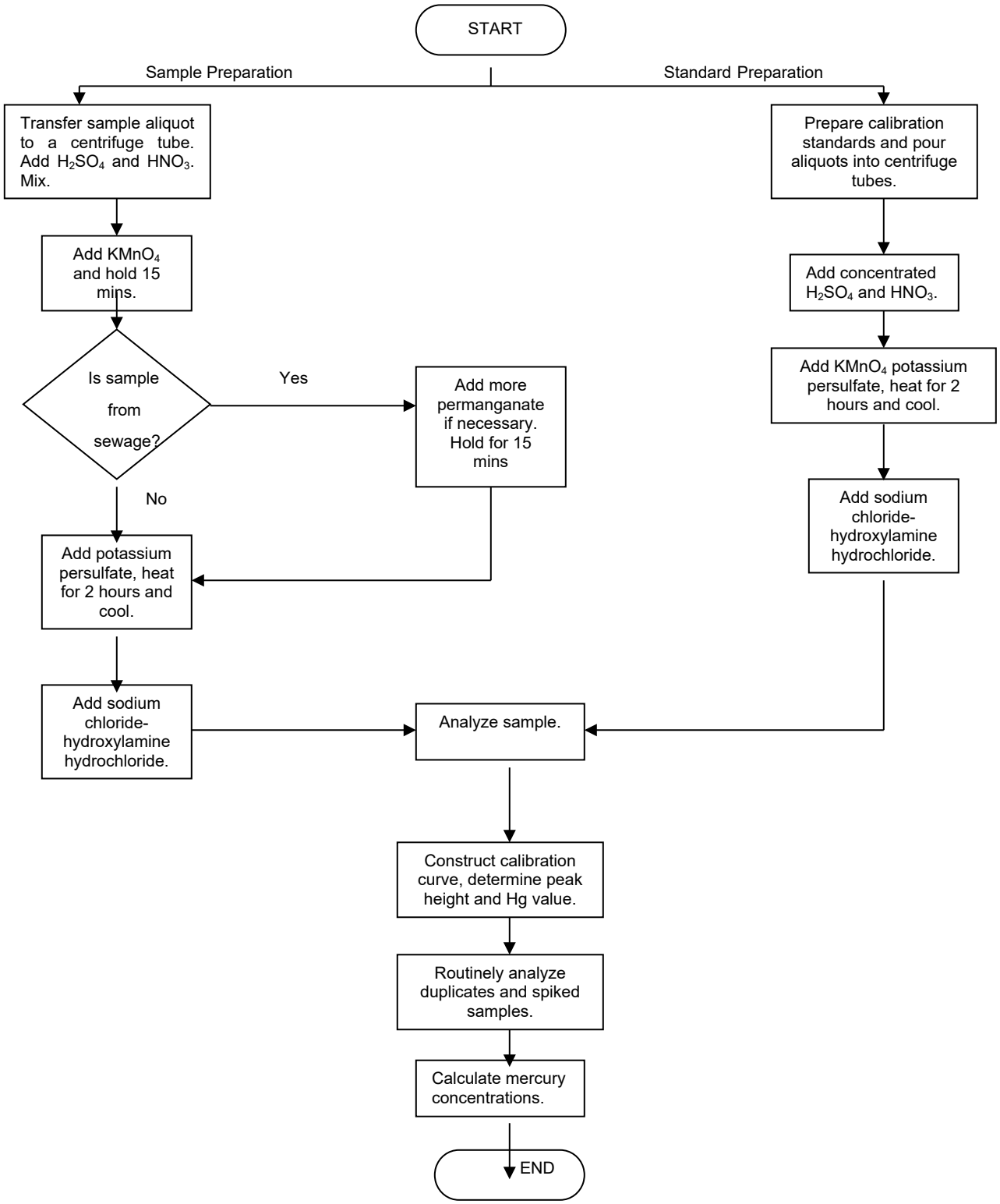
SOP/1797 Waste Management and Disposal SOP

16. Attachments

Figure 1: Method 7470A Flow Chart

Figure 1

Method 7470A Flow Chart



Mercury in Solid or Semisolid Waste
(Manual Cold-Vapor Technique)

Reference Method No.: **EPA 7471B**

Reference: SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, February 2007.

1. Scope and Application

Matrices: Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

Definitions: Refer to Alpha Analytical Quality Manual.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the Mercury Analyzer and in the interpretation of Mercury data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability..

2. Summary of Method

Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.1 Method Modifications from Reference

Alpha analyzes only one 0.3g aliquot of sample. The original method does not address the automated instrument procedure. A reduced volume of sample is digested in disposable digestion tubes on a hot block digestor.

3. Reporting Limits

The reporting limit for this method is 0.08mg/Kg.

4. Interferences

Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL).

Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

Because mercury vapor is toxic, precaution must be taken to avoid its inhalation.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples may be collected in plastic or glass containers.

6.2 Sample Preservation

None.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples are stored under refrigeration at 4°C and analyzed as soon as possible after collection. The samples have a 28-day holding time from the time of collection.

7. Equipment and Supplies

7.1 Instrumentation:

Perkin Elmer FIMS 100 Atomic absorption spectrophotometer: Use instrument settings recommended by the manufacturer. The PE FIMS is designed specifically

for the measurement of mercury using the cold-vapor technique with BOC (background offset correction) performed by a survey scan prior to each sample introduction. PE S10 autosampler is coupled to the instrument.

Cetac M-6100 Atomic absorption spectrophotometer: Use instrument settings recommended by the manufacturer. This instrument employs a reference cell off-set correction and full automation through the CETAC software. A Cetac ASX-260 autosampler is coupled to the instrument.

7.2 Hot Block Digestor: Environmental Express, 54 position, capable of maintaining a temperature of 95°C +/-3°C.

7.3 Graduated cylinder. Rinse once with 50% Nitric Acid, then rinse with reagent water prior to use.

7.4 Volumetric Flasks, Class A, various volumes. Rinse once with 50% Nitric Acid, then rinse with reagent water prior to use.

7.5 Polypropylene Digestion Vessels: 50 mL volume, with plastic screw caps

7.6 Pump Tubing: Environmental Express, three stop and two stop tubing in various IDs.

7.7 PTFE membranes: Pall TF1000 disks

7.8 Dilution vials: 20mL capacity, used when making analytical dilutions.

7.9 Laboratory Wipes

7.10 Compressed Air

7.11 Whatman 41 or equivalent filter paper

7.12 Eppendorf pipets: Accurate means to make trace standards

8. Reagents and Standards

8.1 Reagent Water: Reagent water is DI water shown to be interference free. All references to water in this method refer to reagent water unless otherwise specified.

8.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

8.3 Concentrated Nitric Acid, (HNO_3): Trace grade. Store at room temperature in the appropriately marked acid cabinet.

8.4 Concentrated Hydrochloric Acid, (HCl): Trace grade. Store at room temperature in the appropriately marked acid cabinet.

8.5 Reductant, Stannous Chloride in 3% HCl: This is the ***reductant*** for the Instrument. In a 1L volumetric flask, add 30mL concentrated trace grade HCl and 11g $SnCl_2 \cdot 2H_20$. Mix to dissolve the solid and bring to volume with reagent water. Store at room temperature, prepare as needed.

8.6 Carrier, Hydrochloric Acid, 3%: This is the ***carrier*** for the instrument. In a 1L volumetric flask, add 30mL concentrated trace grade HCl (Section 8.4). Bring to volume with reagent water. Store at room temperature, prepare as needed.

8.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water. Store at room temperature.

8.8 Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride in reagent water and dilute to 100 mL. Store at room temperature.

8.9 Mercury stock solution, 1000ppm: This solution is purchased commercially prepared with a certificate of analysis. Three solutions are purchased, each from a different source. Store at room temperature. Expires according to manufacturer's specifications.

8.9.1 10ppm Mercury Stock Standard: To a 100mL volumetric flask, add 5mL of concentrated HNO_3 and 1.0mL of 1000ppm Mercury Stock Solution (Section 8.9). Bring to volume with reagent water. Store at room temperature. Expires one month from date of preparation.

8.9.1.1 0.1ppm Mercury Working Stock / Matrix Spike Solution: To a 500mL volumetric flask, add 5mL of concentrated HNO_3 and 5 mL of 10ppm Mercury Stock Standard (Section 8.9.1). Bring to volume with reagent water. Store at room temperature. Expires one week from date of preparation.

8.9.2 10ppm Mercury ICV Stock Standard: To a 100mL volumetric flask, add 5mL of concentrated HNO_3 and 1.0mL of Mercury Stock Solution (Section 8.9, from an alternate source than that used in Section 8.9.1). Bring to volume with reagent water. Store at room temperature. Expires one month from date of preparation.

8.9.2.1 0.3ppm Mercury ICV Working Stock: To a 100mL volumetric flask, add 5mL of concentrated HNO_3 and 3.0mL of 10ppm Hg ICV Stock Standard (Section 8.9.2). Bring to volume with reagent water. Store at room temperature. Expires one week from date of preparation.

8.9.3 10ppm Mercury LCS Stock Standard: To a 100mL volumetric flask, add 5mL of concentrated HNO_3 and 1.0mL of 1000ppm Mercury Stock Solution (Section 8.9, from an alternate source than that used in Sections 8.9.1 and 8.9.2). Bring to volume with reagent water. Store at room temperature. Expires one month from date of preparation.

8.9.3.1 0.1ppm Mercury LCS Working Stock: To a 100mL volumetric flask, add 5mL of concentrated HNO_3 and 1.0mL of 10ppm Mercury LCS Stock Standard (Section 8.9.3). Bring to volume with reagent water. Store at room temperature. Expires one week from date of preparation.

8.10 SRM: Purchased from ERA in 300-500g lots.

9. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

The Method Blank consists of the 0ppm standard as prepared in Section 10.1.2.1.1. Analyze one Method Blank per analytical batch of twenty samples or less. The Method Blank must be less than the Reporting Limit (RL). See Section 12.1 for corrective action.

9.1.1 PBS

A preparation blank is analyzed once per batch of twenty samples or less. It is prepared in the same manner as the 0ppm standard (Section 10.1.2.1.1). The PBS must be recovered within ± 0.2 µg/L.

9.1.2 ICB

The ICB is analyzed after the ICV, and is prepared in the same manner as the 0ppm standard (Section 10.1.2.1.1). The ICB must be recovered within ± 0.2 µg/L.

9.1.3 CCB

The CCB is analyzed after the CCV. It is prepared in the same manner as the 0ppm standard (Section 10.1.2.1.1). The CCB must be recovered within ± 0.2 µg/L.

9.2 Laboratory Control Sample (LCS)

The LCS is analyzed once per each analytical batch of twenty samples or less. It is prepared in the same manner as in Section 10.1.2.3. The LCS must be recovered within 80 – 120% of the true value. See Section 12.3 for corrective action.

9.3 Initial Calibration Verification (ICV)

The ICV is analyzed after the calibration curve. It is prepared in the manner specified in Section 10.1.2.2. The ICV must be recovered within ± 10% of the true value. See Section 12.2 for corrective action.

9.4 Continuing Calibration Verification (CCV)

The CCV is analyzed after every ten analytical samples. It is prepared in the same manner as the 5.0ppb calibration standard (Section 10.1.2.1.5). The CCV must be recovered within 20% of the true value. See Section 12.2 for corrective action.

9.5 Matrix Spike

Analyze one matrix spike per twenty or less analytical samples. The recovery of the matrix spike must be between 80 – 120%. Calculate percent recovery using Section 11.2.

If the recovery of the matrix spike is out of range, a post-analytical spike is analyzed. Prepare the post analytical spike by adding 5mL of 0.010ppm Calibration Standard (Section 10.1.2.1.6) and 5mL of the sample digestate to a 50mL centrifuge tube for a final concentration of 0.005mg/L. Analyze the post spike as outlined in Section 10.3.

Calculate the post spike concentration as follows:

Post Analytical Spike Sample Concentration (mg/L) =

[Sample Concentration (mg/L) x (0.5)] + 0.005mg/L

The percent recovery of the post-analytical spike must be between 75 – 125%.

See Section 12.4 for corrective action.

9.6 Laboratory Duplicate

Analyze one sample in duplicate per twenty or less analytical samples. The RPD between the sample and its duplicate must be ≤ 20% (as calculated in Section 11.3). See Section 12.5 for corrective action.

9.7 Method-specific Quality Control Samples

None

9.8 Method Sequence

- Sample preparation
- Sample digestion
- Standards preparation:
  - Calibration standards
  - ICV standard
  - LCS standard
- Standards digestion
- Analysis of calibration standards
- Generation of calibration curve
- Analysis of samples and standards:
  - ICV
  - ICB
  - analytical samples
  - CCV
  - CCB
  - analytical samples
  - CCV
  - CCB
  - etc.

10. Procedure

10.1 Equipment Set-Up

10.1.1 Sample preparation: Weigh a 0.3-g portion of untreated and homogenized sample and place in the bottom of a polypropylene digestion vessel. Record the weight in the laboratory notebook. NOTE: When preparing the batch, include one sample duplicate aliquot to be prepared in the same manner.

Add 2.5 mL of reagent water and 2.5 mL of aqua regia (Section 8.2). Heat 2 min on a hot block at 95°C +/-3°C. Cool; then add 15 mL reagent water, and 7.5 mL potassium permanganate solution (Section 8.7) to the digestion vessel. Wait 15 minutes to be sure the potassium permanganate is not exhausted (purple color disappears), if it does add additional potassium permanganate to all samples and QC until stable. Mix thoroughly and place in the hot block for 30 min at 95°C +/-3°C. Cool and add 3 mL of sodium

chloride-hydroxylamine hydrochloride (Section 8.8) to reduce the excess permanganate.

CAUTION: Perform this addition under a hood, as Cl_2 could be evolved.

Bring up to a final volume of 50 mL with reagent water. Continue as described under Section 10.3.1.

10.1.2 Standard preparation: Standard preparation is performed each time samples are digested.

10.1.2.1 Calibration Standards

10.1.2.1.1 0 ppb: Add 10mL of reagent water to a polypropylene digestion vessel. This aliquot may be used for the CCB. Another separate aliquot is prepared for use as the ICB and the diluent for any samples with concentration greater than 90% the highest calibration standard used to determine the linear range.

10.1.2.1.2 0.5ppb: Add 10 mL of reagent water to a polypropylene digestion vessel. Using a volumetric pipet, add 0.25 mL of 0.1ppm Mercury Working Stock (Section 8.9.1.1) to the digestion vesel.

10.1.2.1.3 1.0ppb: Add 10 mL of reagent water to a polypropylene digestion vessel.. Using a volumetric pipet, add 0.5 mL of 0.1ppm Mercury Working Stock (Section 8.9.1.1) to the digestion vessel.

10.1.2.1.4 2.0ppb: Add 10 mL of reagent water to a polypropylene digestion vessel.. Using a volumetric pipet, add 1.0mL of 0.1ppm Mercury Working Stock (Section 8.9.1.1) to the digestion vessel.

10.1.2.1.5 5.0ppb/CCV: Add 10 mL of reagent water to a polypropylene digestion vessel.. Using a volumetric pipet, add 2.5 mL of 0.1ppm Mercury Working Stock (Section 8.9.1.1) to the digestion vessel.

10.1.2.1.6 10ppb: Add 10 mL of reagent water to a polypropylene digestion vessel.Using a volumetric pipet, add 5.0 mL of 0.1ppm Mercury Working Stock (Section 8.9.1.1) to the digestion vessel.

10.1.2.1.7 20ppb: Add 10 mL of reagent water to a polypropylene digestion vessel.Using a volumetric pipet, add 10.0 mL of 0.1ppm Mercury Working Stock (Section 8.9.1.1) to the digestion vessel.

10.1.2.2 ICV Standard, 3.0ppb: This standard is used for calibration verification.

Add 10.0 mL of reagent water to a digestion vessel. Using a volumetric pipet, add 0.5 mL of 0.3ppm Mercury Working Stock (Section 8.9.2.1) to the digestion vessel. Digest the ICV Standard as in Section 10.1.3.

10.1.2.3 LCS Standard, 1.0ppb: This standard is prepared and analyzed with each analytical batch.

Add 5.0mL of reagent water to a digestion vessel. Add 0.15g of SRM (Section 8.10). Digest the LCS Standard as in Section 10.1.3.

10.1.2.4 Matrix Spike, 0.001mg/L: Weigh two aliquots of the sample designated to be the batch matrix spike.

Add 10.0 mL of the reagent water to the digestion vessel containing the weighed sample aliquot. Add a 0.5 mL aliquot of 0.1ppm Mercury LCS Working Stock (Section 8.9.3.1). Digest the MS as in Section 10.1.3.

10.1.3 Standard Digestion:

To each standard (Sections 10.1.2.1 through 10.1.2.3), add 2.5 mL of reagent water and 2.5 mL of aqua regia (Section 8.2) and heat 2 min on the hot block at 95°C +/- 3°C. Allow the standard to cool; add 15 mL reagent water and 7.5 mL of $KMnO_4$ solution (Section 8.7) to each bottle and return to the hot block for 30 min. Cool and add 3 mL of sodium chloride-hydroxylamine hydrochloride solution (Section 8.8) to reduce the excess permanganate. Bring up to final volume of 50 mL with reagent water, continue as described in Section 10.3.3.

Note: Alternate volumes of standards may be made base on need as long as they are made with the same proportions as describe above.

10.2 Initial Calibration

Construct a calibration curve by plotting the absorbances of prepared standards (Section 10.1.2) versus micrograms of mercury. (See Section 11.1.) Determine the peak height of the unknown from the absorbance maxima on the spectrometer, and read the mercury value from the standard curve.

The curve correlation coefficient (cc) must be greater than or equal to 0.995 in order for the curve to be linear. If the correlation coefficient is less than 0.995, find and correct the problem. When the problem has been corrected, re-analyze either the previous standards or new standards. When the curve has generated an acceptable cc, then the analysis can continue with the ICV/ICB.

Analyze an Initial Calibration Verification Standard (ICV) (Section 9.3), an Initial Calibration Blank sample (ICB) (Section 9.1.2) at the start of the analytical run. The results for the ICV must be within 10% of the true value. If results are outside this range, refer to Section 12.2 for corrective action.

10.3 Equipment Operation and Sample Processing

10.3.1 Instrument Setup

10.3.1.1 Turn the instrument on. The autosampler will initialize itself.

10.3.1.2 Choose the instrument software from the desktop menu. The autosampler will initialize again.

FIMS 100 NOTE: The instrument must be turned on before the application is started. Otherwise, an error message will result.

10.3.1.3 Enter the appropriate fields for sample identification, and data storage.

10.3.1.4 Fill the carrier and reductant bottles.

10.3.1.4.1 The Carrier is 3% HCl (Section 8.6).

10.3.1.4.2 The Reductant is 1.1% $SnCl_2$ in 3% HCl (Section 8.5).

10.3.1.5 Allow the instrument to warm up while clearing samples. Samples that are cloudy or with particulate present after clearing must be filtered through Whatman 41 filter paper (Section 7.11) before analysis.

10.3.1.6 Place carrier uptake line and reductant uptake line.

10.3.1.7 Load carrier and reductant lines into pump magazines

10.3.1.8 Load the two waste lines into the pump magazines below the roller.

10.3.1.9 Lock the magazines into place.

FIMS100 only:

10.3.1.10 Remove the cap from the liquid/vapor separator and wipe dry with a Lab Wipe (Section 7.9). Compressed air (Section 7.10) through the vapor transfer line to dry it out.

10.3.1.11 Place a PTFE membrane (Section 7.7), rough side up, in the liquid/vapor separator; replace the cap and reattach the vapor transfer line to the sample absorption cell.

10.3.1.12 Adjust the gas flow by turning the black knob below the air flow meter to obtain a reading of just over 50.

10.3.2 Calibration and Sample Analysis

10.3.2.1 The instrument will now run the calibration standards; verify a CC of 0.995 or better before proceeding with the ICV and ICB. Ten analytical samples, a CCV and CCB, ten analytical samples, CCV, CCB, etc. The CCBs and CCVs must be recovered within the proper ranges (Sections 9.4 and 9.1.3) for analysis to continue.

10.3.2.2 If the sample result is beyond 90% of the concentration of the highest point on the calibration curve or LDR study used to establish the linear range, dilute the sample extract with a portion of one of the prepared blanks (ICB, CCB or PBS) to produce an analytical result that is within the range.

10.3.3 Instrument Shut Down

10.3.3.1 When analysis is complete place reagent uptake lines in a beaker of reagent water.

10.3.3.1.1 Continue to run the pumps for several minutes to flush reagents out of the lines.

10.3.3.1.2 Continue to run the pumps for several minutes to flush reagents out of the lines.

10.3.3.2 Pull the reagent uptake lines out of the reagent water beaker to allow the pump to draw air through the lines.

10.3.3.3 Unlock the top and bottom pump magazines and remove tubing from the magazines.

10.3.3.4 Exit from the software application.

10.3.3.4.1 Dump the samples and instrument waste in the Metals/WetChem waste drum located in the transfer room.

10.4 Continuing Calibration

After every 10 samples, analyze a Continuing Calibration Verification Standard (CCV), and a Continuing Calibration Blank sample (CCB). Determine the concentrations from the calibration curve. The results for the CCV must be within 20% of the true value.

10.5 Preventive Maintenance

Preventative maintenance is conducted per the manufacturer's instructions. All preventative maintenance is recorded in the Instrument Maintenance Logbook.

11. Data Evaluation, Calculations and Reporting

11.1 Calculate Mercury Concentration From the Daily Calibration Curve

The curve is generated utilizing a straight-line equation defined as:

$$A = k_1 + k_2C$$

Where:

A = Average peak height of the sample/standard integrations
C = Sample/Standard Concentration, µg/L
k_1 = y-intercept
k2 = slope

The instrument will plot peak height against concentration (µg/L). The result is generated in µg/L. This value is divided by 1000 to convert the units to mg/L. The mg/L units are converted to mg/Kg by multiplying by L/Kg. A dilution factor (DF) is applied if necessary. The Result is then divided by the % Total Solids prior to release to the client.

$$\text{Result, mg/Kg} = (\text{concentration, µg/L}) \times (1\text{mg}/1000\mu\text{g}) \times (\text{DF}) \times (\text{L/Kg})$$

Where:

$$\text{L/Kg} = \frac{\text{Final volume of digestate, in L}}{\text{Weight of original sample, in Kg}}$$

11.2 Calculate Percent Recovery for the Matrix Spike corrected for concentrations measured in the unfortified sample. Percent recovery is calculated using the following equation:

$$\%\ \text{Recovery} = \frac{(Cm - C)}{S} \times 100$$

Where:

Cm = measured Mercury in the fortified sample
C = measured native mercury sample concentration
S = concentration equivalent of spike added to sample

11.3 Calculate the Relative Percent Difference (RPD) for each Duplicate of the initial quantitated concentration (IC) and duplicate quantitated concentration (Dc) using the following formula:

$$RPD = \frac{|(IC - Dc)|}{\{(IC + Dc) / 2\}} \times 100$$

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

12.1 Method Blank Failure

When a prep blank mercury concentration is $\geq$10% of the mercury concentration determined for any associated sample, or is greater than 2.2x the MDL value (whichever is greater), the entire batch associated with the prep blank must be redigested.

12.2 ICV / CCV Failure

If the ICV %Recovery is outside of acceptance criteria, analysis is terminated until the problem is found and corrected. If the CCV %Recovery is outside of acceptance criteria, all samples analyzed since the last acceptable CCV must be reanalyzed following correction of the problem.

12.3 LCS Failure

If the LCS is not recovered within acceptance criteria, the associated batch and another LCS must be redigested (Section 10.1).

12.4 Matrix Spike/Post Digestion Spike Failure

If the recovery of the matrix spike is outside of the acceptance criteria of 80 – 120%, a post digestion spike is performed (Section 9.5). If the post digestion spike is beyond 75 – 125%, the sample and its spike are redigested (Section 10.1).

12.5 Duplicate Failure

If the RPD between the sample and its duplicate is greater than 20%, visually evaluate the sample matrix. If the sample matrix appears clean, the sample and its duplicate are removed from the batch and redigested (Section 10.1). If the matrix appears problematic, the sample digestate may be diluted and reanalyzed, or a narrative included with the data to explain the matrix problem.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP 1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP 1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/1732 DL/LOD/LOQ Generation

SOP/1739 IDC/DOC Generation

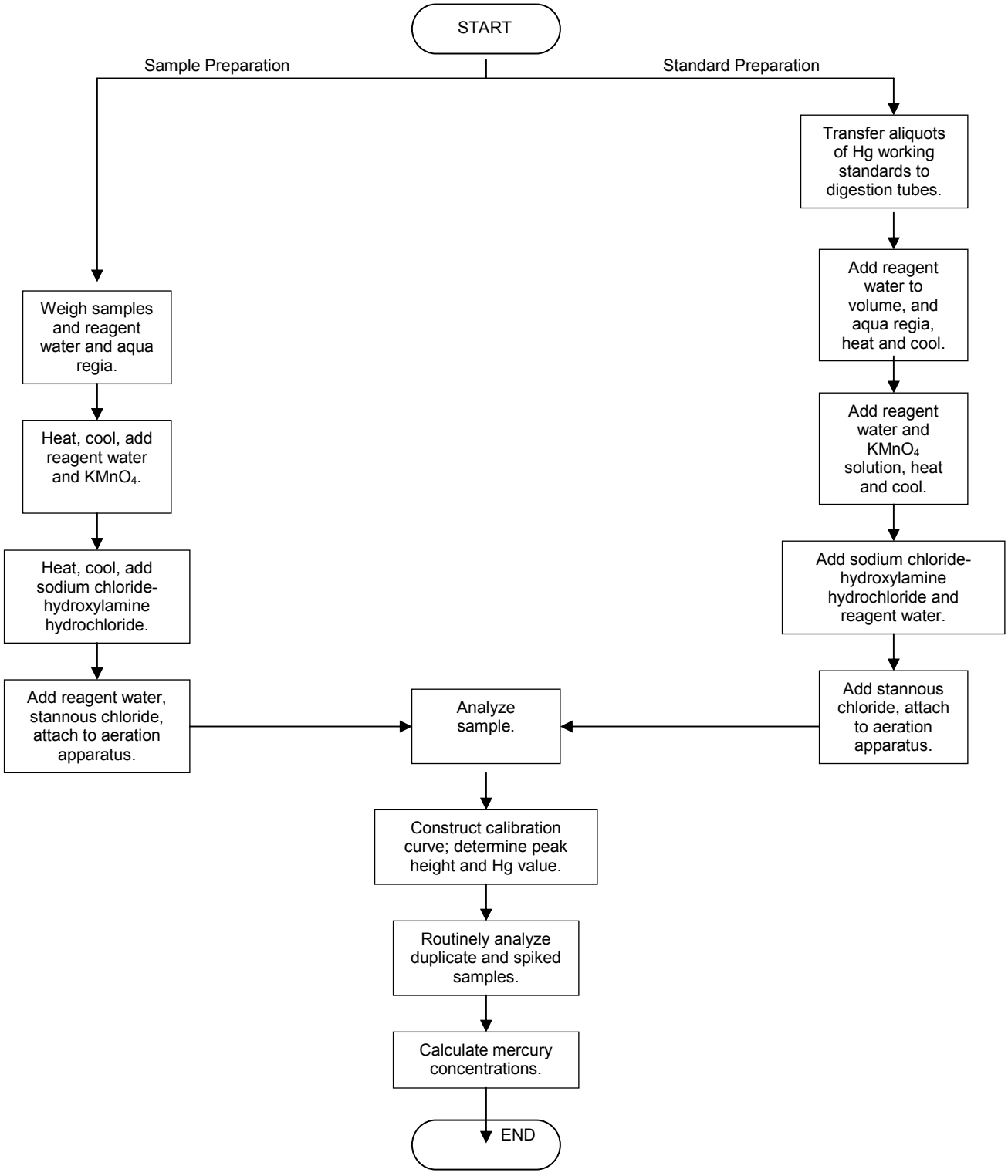
SOP/1797 Waste Management and Disposal SOP

16. Attachments

FIGURE 1: Flow Chart for Method 7471B

Figure 1

Method 7471B Flow Chart



Inductively Coupled Plasma - Atomic Emission Spectrometry

Reference Method No.: **Method 6010D** SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update V, July, 2014.

SM 2340B, Hardness by Calculation, Standard Methods for the Examination of Water and Wastewater, APHA-AWWA-WPCF, 21st Edition, 1997.

1. Scope and Application

Matrices: Digestates from all matrices.

Definitions: See Alpha Laboratories Quality Manual Appendix A

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludge, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion unless chemical interferences are suspected. Samples which are not digested are matrix matched with the standards. Refer to Metals Preparation SOPs for the appropriate digestion procedures.

Table 1 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the recommended analytical wavelengths for the elements in clean aqueous matrices. Table 3 lists the Reported Detection Limits. The reported detection limit data may be used to estimate instrument and method performance for other sample matrices. Elements other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest (see Section 9) is demonstrated.

Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is made by one of the following laboratory personnel before performing the modification: Area Supervisor, Metals Manager, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

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2. Summary of Method

Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used must be as free as possible from spectral interference and must reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 4.0 must also be recognized and appropriate corrections made; tests for their presence are described in Section 9.7. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

This SOP includes the manual calculations for Total Hardness and Calcium Hardness, according to SM 2340B.

2.1 Method Modifications from Reference

None.

3. Reporting Limits

Refer to Table 3 for method Reporting Limits.

4. Interferences

4.1 Spectral

Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for

routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans must be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

4.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

4.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

4.1.4 When using inter-element correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that each instrument may exhibit somewhat different levels of interference. The interference effects must be evaluated for each individual instrument since the intensities will vary.

Major known interferences are Fe, Al, Ca, Mg, V, Ni, Cu, and Cr. To minimize any of these interferences, every analyte is analyzed on each instrument at or near its linear range and corrected for these interferences. This is done on an annual basis, and data is kept on file.

4.1.5 Inter-element corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Inter-element corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear must be avoided when practical. Inter-element corrections that constitute a major portion of an emission signal may not yield accurate data. Users must not forget that some samples may contain uncommon elements that could contribute spectral interferences.

4.1.6 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

4.1.7 The primary wavelength for each analyte is based upon the instrument manufacturer's recommendations. An alternate wavelength is chosen if there is an indication of elevated background or overlap of another spectral wavelength. The wavelength for each analyte must be as free from interferences as possible.

4.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution must fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change must be determined and corrected and the correction factor updated. The interference check solutions must be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

4.1.9 When inter-element corrections are applied, their accuracy must be verified, daily, by analyzing the spectral interference check solution. The correction factor or multivariate correction matrices tested on a daily basis. All inter-element spectral correction factors or multivariate correction matrices are verified and updated when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. The standard solution must be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

4.1.10 When inter-element corrections are <u>not</u> used, verification of absence of interferences is required.

4.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits, files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte

instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

4.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is >20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

4.2 Physical

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, using a peristaltic pump, use of an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers. The test described in Section 10.3.4.1 will help determine if a physical interference is present.

4.3 Chemical

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Additionally, if filtered samples are found to have an organic or sulfur like odor they are processed by heating after the addition of the acids to matrix match. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4 Memory

Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build-up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences must be recognized within an analytical run and suitable rinse times must be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample must be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit must be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If memory interference is suspected, the sample must be reanalyzed after a rinse

period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

4.5 Other Interferences

4.5.1 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations must be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in plastic bottles.

6.2 Sample Preservation

If samples are for soluble metals analysis, filtration must take place prior to preservation with 1:1 HNO3 to a pH < 2. Soluble samples must be held at pH < 2 for at least 24 hours prior to digestion if not preserved at the time of filtration. Samples for total metals analysis are preserved with 1:1 HNO3 to a pH < 2. Samples must be pH <2 for at least 24 hours prior to digestion if not preserved at the time of collection.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples to be analyzed for soluble metals, that have not been filtered, must be filtered and preserved within 24 hours of sample collection.

Preserved samples have a hold time of 6 months, and are stored at ambient temperature.

7. Equipment and Supplies

7.1 Inductively coupled argon plasma emission spectrometer:

- **Thermo Scientific ICAP Duo 6500 (Trace7)**

7.1.1 Computer-controlled emission spectrometer with background correction.

7.1.2 Radio-frequency generator compliant with FCC regulations.

7.1.3 Optional mass flow controller for argon nebulizer gas supply.

7.1.4 Optional peristaltic pump.

7.1.5 Optional Autosampler.

7.1.6 Argon gas supply - high purity.

7.2 Volumetric flasks of suitable precision and accuracy.

7.3 Volumetric pipets of suitable precision and accuracy.

8. Standards and Reagents

Reagent semiconductor and/or trace grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable.

8.1 Hydrochloric acid (conc), HCl. Stored at room temperature in acid resistant cabinet. Expiration date if defined by vendor.

8.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL DI water and dilute to 1 liter in an appropriately sized beaker. Stored at room temperature in polypropylene bottle, expiration date if defined by vendor..

8.3 Nitric acid (conc), HNO_3. Stored at room temperature in acid resistant cabinet. Expiration date if defined by vendor.

8.4 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL DI water and dilute to 1 liter in an appropriately sized beaker. Stored at room temperature in polypropylene bottle, expiration date if defined by vendor..

8.5 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

8.6 Standard stock solutions may be purchased or prepared from ultra- high purity grade chemicals or metals (99.99% pure or greater). All stock standards are ordered through ISO and American Association for Lab Accreditation vendors. All standards are in aqueous solutions and are generally at concentrations of 1000ppm and 10,000ppm.

8.7 Mixed calibration standard solutions

Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Care must be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to HDPE or polypropylene bottles for storage. Fresh mixed standards must be prepared, as needed, with the realization that concentration can change on aging as evidenced by failures in the ICV.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration must be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.
Additionally, sulfur standards are stand-alone single element standards and therefore are not to be combined in a mixed calibration standard solution.

8.8 Blanks

Three types of blanks are required for the analysis for samples. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing. The rinse blank is used to flush the system between all samples and standards.

8.8.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations (see Sections 10.2 and 10.4). Refer to Section 10.4.1.2 for acceptance criteria and/or corrective actions.

8.8.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis. Refer to Section 9.1 for acceptance criteria and/or corrective actions.

8.8.3 The rinse blank consists of HNO_3 (1% or 2%) (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

8.9 The Initial Calibration Verification Standard (ICV) and the Continuing Calibration Verification Standard (CCV)

These ICV is prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard at a concentration at or near the mid-point of the calibration curve. The CCV is prepared from the same source as the calibration standards and must be at a concentration near the mid-point of the calibration curve.

8.10 Low Level of Quantification, (LLOQ)

The LLOQ is initially verified by the analysis of at least 7 replicate samples, spiked at the LLOQ and processed through all preparation and analysis steps of the method at or below the lowest calibration point. The mean recovery and relative standard deviation of these samples provide an initial statement of precision and accuracy at the LLOQ. In most cases the mean recovery should be +/- 35% of the true value and RSD should be < 20%. In-house limits may be calculated when sufficient data points exist. Monitoring recovery of LLOQ over time is useful for assessing precision and bias.

Ongoing LLOQ verification, at a minimum, is on a quarterly basis to validate quantitation capability at low analyte concentration levels. This verification may be accomplished either with clean control material (e.g., reagent water, method blanks. Optimally, the LLOQ should be less than the desired regulatory action levels based on the stated project-specific requirements.

8.11 Spectral Interference Check Solution

These solutions are prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Analysts are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests.

Single element interference checks - At a minimum, single element SIC checks must be performed for the following elements: Aluminum 500mg/L; Boron 50mg/L, Barium, 50mg/L, Calcium 500mg/L; Copper 50mg/L; Iron 200mg/L; Magnesium 500mg/L; Manganese 50mg/L; Molybdenum 20mg/L; Sodium 1000mg/L; Nickel 20mg/L; Selenium 20mg/L; Silicon 200mg/L; Tin 20mg/L; Vanadium 20mg/L; Zinc 20mg/L The absolute value of the concentration observed for any unspiked analyte in the single element SIC checks must be less than two times the analytes' LLOQ.

The concentration of the SIC checks are suggested, but become the highest concentration allowed in a sample analysis, and cannot be higher than the highest established linear range. Samples with concentrations of elements higher than the SIC check must be diluted until the concentration is less than the SIC check solution. Note that reanalysis of a diluted sample is required even if the high concentration element is not required to be reported for the specific sample, since the function of the SIC check is to evaluate spectral interferences on other elements. The single element SIC checks are performed when the instrument is setup and periodically (at least once every 6 months) thereafter.

Mixed element interference check - The mixed element SIC solution is analyzed at least once per day, immediately after the initial calibration. The concentration measured for any target analytes must be less than +/- the LLOQ. If this criterion is not met then sample analysis may not proceed until the problem is corrected, or alternatively the LLOQ may be raised to twice the concentration observed in the SIC solution. The only exceptions are those elements that have been demonstrated to be contaminants in the SIC solutions These may be present up to the concentration documented plus the LLOQ.

Mixed element SIC solution: Aluminum, 500mg/L; Calcium, 500mg/L; Iron, 200mg/L; Magnesium, 500mg/L

8.12 Ongoing Low Level of Quantification, (LLOQ)

Ongoing LLOQ verification, at a minimum, is on a quarterly basis to validate quantitation capability at low analyte concentration levels. This verification may be accomplished either with clean control material (e.g., reagent water, method blanks. Optimally, the LLOQ should be less than the desired regulatory action levels based on the stated project-specific requirements.

8.13 Internal Standard

The internal standard consists of a multi-element solution; each internal standard covers a range of the spectrum (low, middle, or high wavelengths) and the elements within that range.

100 mg/L Ce

20 mg/L Cs

2.0 mg/L Lu

Note: The standard is used to monitor instrument fluctuations including but not limited to nebulization efficiency, plasma variations, environmental temperature changes, peristaltic pump pulsations, etc. Therefore, the solution used to start an analysis calibration cannot be added to or changed out during analysis without requiring subsequent full recalibration.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample.

The method blank results must be less than ½ of the LLOQ for all analytes of concern. If the results of the method blank exceed the RDL for any analyte, perform re-analysis of a new aliquot of the method blank.

If the results continue to exceed the RDL, proceed as follows:

If all of the samples for the analyte are non-detected, and the method blank is at or above the RDL, no action is required.

If one or more associated samples for that analyte have positive results at or above the RDL, those samples must be considered to be out of control, and are re-digested and reanalyzed.

9.2 Laboratory Control Sample (LCS)

Analyze one LCSW/SRM per sample batch. A LCS/SRM sample is a spiked volume of reagent water that is brought through the entire preparation and analytical process. The LCSW must have a % Recovery of ± 20% within the actual value or within vendor control limits (95% confidence limits) for the solid SRM.

If the LCSW or SRM % Recovery is outside the acceptable limits as stated in Table 2, or outside any vendor control limits, the LCS is rerun once. If upon reanalysis the LCS is still out

of control, the failed analytes are re-prepped and re-analyzed. Otherwise, a nonconformance report form is raised to document the exact problem and this form is then authorized by the QA/QC Director and/or the Laboratory Manager(s).

9.3 Initial Calibration Verification (ICV)

For all analytes and determinations, the laboratory must analyze an ICV (Section 8.9), and a calibration blank (ICB, Section 8.8.1), immediately following daily calibration. The results of the ICV are to agree within 10% of the expected value; if not, re-analyze once, if still failing terminate the analysis, correct the problem, and recalibrate the instrument.

9.4 Continuing Calibration Verification (CCV)

A calibration blank (CCB, Section 8.8.1) and a calibration verification standard (CCV, Section 8.9) must be analyzed after every tenth sample and at the end of the sample run. Analysis of the calibration verification (CCV) must verify that the instrument is within 10% of the calibration with the relative standard deviation < 5% from replicate (minimum of two) integrations.

Immediate corrective action for a failing CCV/CCB includes reanalyzing the failing standard. If the standard passes the second time then the analysis may be continued. The batch sheet is noted. If the standard fails again, instrument maintenance must be performed and the CCV/CCB standard is reanalyzed. If the standard passes, then all samples run after the last passing CCV/CCB pair must be re-analyzed.

If the standard fails after instrument maintenance, the instrument is recalibrated. A new ICV/ICB is performed, and all previous data after the last passing CCV/CCB is reanalyzed.

9.5 Matrix Spike

Analyze matrix spike samples at a frequency of one per matrix batch. The matrix spike is the same solution as used for the LCS (Table 4). A matrix spike sample is a sample brought through the entire sample preparation and analytical process.

9.5.1 The percent recovery is to be calculated as follows:

$$\% \text{ Recovery} = \frac{MS - S}{C} \times 100$$

where:

MS = Matrix Spike value
S = Sample value.
C = Concentration of the Spiking solution.

9.5.2 If the Matrix Spike falls outside of the limits as stated in Table 2, or outside any historical documentation for analytes of interest a post analytical spike is performed for the failed analytes. The same sample from which the MS/MSD aliquots were prepared should be spiked with a post digestion spike at a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. The acceptable % Recovery of the post analytical spike is 80-120%. A nonconformance is noted in the LIMS and approved in secondary peer review and/or by the Metals Manager.

9.5.3 If the Post Spike fails the dilution test should be performed**.** If the analyte concentration is sufficiently high (minimally, a factor of 25 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ± 20% of the original determination. If not, then a chemical or physical interference effect should be suspected.

9.6 Laboratory Duplicate

A duplicate sample is analyzed once per matrix batch. This sample is brought through the entire sample preparation and analytical process.

9.6.1 The relative percent difference between duplicate determinations is to be calculated as follows:

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

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (replicate).

9.6.2 If the Duplicate falls outside of the limits as stated in Table 2, or outside any historical documentation and the concentrations of the failing analytes are less than 5x the RL or a matrix interference is found a nonconformance is noted in the LIMS and approved in secondary peer review and/or by the Metals Manager.

9.7 Method-specific Quality Control Samples

9.7.1 Spectra Interference Check Standard

A mixed check solution is analyzed once daily (section 8.11). One solution (SIC) has only elevated concentrations of Fe, Al, Ca, Mg to ensure no interferences occur. The concentrations of the analytes of interest must have an absolute value of the LLOQ. This solution is analyzed at the beginning of the first analytical run of the day.

The high level interferences are not evaluated for recovery. If the SIC fails take corrective action which may include re-evaluation of the inter-element correction values (IECs) after running single element SIC. The instrument calibration routine must then be performed and confirmed by the ICV/ICB pair and the SIC re-analyzed before proceeding with analysis. Otherwise, the nonconformance issue is raised to the Department Supervisor and/or the QA Department.

9.7.2 Internal Standard

The internal standards are added prior to the nebulizer and corrects for intensity differences in the instrument response between the standard's and sample's matrix. They are monitored for any variation in response during the sample analyses and used to ratio the sample response to the internal standard response of the calibration blank. The ratio is applied to compensate for instrument conditions in the plasma or nebulization caused by the matrix. The internal standard is monitored for 50-150% recovery or laboratory generated control ranges difference from the calibration blank IS response to ensure the proper functioning of the internal standard introduction system and matrix interferences. If an injection falls outside of this acceptance range the sample or QC check is rerun once to check for an introduction error.

If a sample continues to fail it's to be run on successive increasing dilutions until the internal standards associated with the elements of interest are within range. If a

QC check fails on the single rerun the analysis is stopped, the root cause investigated, corrected and the instrument re-calibrated/verified. The analysis begins again with all samples that were run after the last acceptable CCV/CCB pair.

9.7.3 LDR Check Solution: A multiple element or single element solution run at a point above the highest calibration standard under the same calibration used to quantify the associated sample data. The LDR check must be within +/-10% of the true value of each element of interest to be considered valid.

9.8 Method Sequence

- Calibration of instrument
- Initial Calibration Verification Standard
- Initial Calibration Blank
- Mixed SIC Solution
- Continuing Calibration Verification Standard
- Continuing Calibration Blank
- 10 samples
- Continuing Calibration Verification Standard
- Continuing Calibration Blank
- 10 Samples
- Continuing Calibration Verification Standard
- Continuing Calibration Blank

10. Procedure

10.1 Equipment Set-up

10.1.1 Sample Preparation

Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been prefiltered and acidified will not need acid digestion. Samples which are not digested must be matrix matched with the standards.

10.1.2 Instrument Set-Up

Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

Startup Procedures

For iCAP Duo 6500

- Turn on power to the chiller
- Click on ThermoSpec Icon; enter analyst initials in login screen
- Click on Plasma icon to start instrument
- Allow to warm up for 30 minutes
- Enter analytical workgroup number (obtained from LIMS) globally under the Instrument menu by selecting Tools, then Options, then Analyst.

- Click on the Sequence tab and enter the sequence by selecting New Autosampler Table, Add Sequence, Add # of spaces.
- Enter the sample locations and IDs
- Press Run Auto-Session button (►) in menu bar.

10.1.2.1 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user.

Operating conditions for axial plasma will vary from 1100 – 1500 watts forward power, 15-19 Liters/min argon coolant flow, 0.5 – 0.7 L/min argon nebulizer flow, 140 – 200 rpm pump rate and a default 1 minute preflush time and 10 second measurement time is recommended for all simultaneous instruments.

10.1.2.2 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

10.1.2.2.1 The Thermo ICP's typically use a Meinhard Nebulizer. The nebulizer flow for each instrument is 1.0 +/- 0.2 mL/min.

10.1.2.2.2 The 6500 Duo instruments automatically perform a wavelength check at start up without user interaction.

10.1.2.2.3 The instrument operating condition finally selected as being optimum must provide the lowest reliable instrument detection limits and method detection limits.

10.1.2.2.4 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and argon pressures must be reoptimized.

10.1.2.2.5 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in the section on interferences. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± ½ LLOQ. The upper control limit is the analyte instrument detection limit. Once established, the entire routine is periodically verified every six months. In between that time, IEC's are done on a need be basis per analyte. Only a portion of the

correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine must be kept on file. Special cases where continual verification is required are described elsewhere.

10.1.2.3 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

10.1.2.3.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit.

10.1.2.3.2 Determination of limits using reagent water MDLs represent a best case situation and do not represent possible matrix effects of real world samples.

10.1.2.3.3 If additional confirmation is desired, reanalyze the seven replicate aliquots on two more non-consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate.

10.1.2.3.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses with 10% of the true value of each element from a concentration standard at the upper limit of the range run on the same calibration as required by the sample responses above the calibration range. The range which may be used for the analysis of samples must be no more than 90% of the resulting data. Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed. The analyst must also be aware that if an inter-element correction from an analyte above the linear range exists, a second analyte where the inter-element correction has been applied may be inaccurately reported.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self-absorption effects. These curves may be used if the instrument allows; however the effective range must be checked and the second order curve fit must have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These curves are much more sensitive to changes in operating conditions than the linear lines and must be checked whenever there have been moderate equipment changes.

10.1.2.4 The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

10.2 Initial Calibration

Calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 8.7. Flush the system with the calibration blank (Section 8.8.1) between each standard or as the manufacturer

recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve consists of a calibration blank, RL standard and a high level standard. Calibration curve verification is accomplished through the analysis of the ICV, ICB and SIC standards.

10.3 Equipment Operation and Sample Processing

10.3.1 For all analytes and determinations, the laboratory must analyze an ICV (Section 8.9), and a calibration blank (ICB, Section 8.8.1), immediately following daily calibration.

A calibration blank (CCB, Section 8.8.1) and a calibration verification standard (CCV, Section 8.9) must be analyzed after every tenth sample and at the end of the sample run. Analysis of the calibration verification (CCV) must verify that the instrument is within 10% of the calibration with the relative standard deviation < 5% from replicate (minimum of three) integrations.

If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable ICV/ICB, or CCV/CCB must be reanalyzed. The analysis data for the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

10.3.2 Rinse the system with the rinse blank solution (Section 8.8.3) before the analysis of each sample. The suggested default rinse time is one minute. Each ICP instrument may establish a reduction in this rinse time through a suitable demonstration.

10.3.3 Dilute and reanalyze samples that exceed the linear range or use a calibrated alternate, less sensitive line for which quality control data is already established.

10.3.4 If less than acceptable accuracy and precision data are generated a series of tests are performed prior to reporting concentration data for analyte elements. At a minimum, these tests should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These tests, as outlined in Sections 10.3.5 and 10.3.6, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

10.3.5 **Post Digestion Spike Addition:** If the sample concentrations are insufficient to perform a dilution test a post digestion spike added to a portion of a prepared sample, or its dilution for the elements failing the matrix spike recoveries must be run, recovery limits equal to 75% to 125% of the known spike value. If the spike is not recovered within the specified limits If the post-digestion recovery fails to meet the acceptance criteria, the sample results must be reported as estimated values

10.3.6 **Dilution Test:** If the analyte concentration is sufficiently high (minimally, a factor of 25 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution must agree within ± 20% of the original determination. Elements that fail the dilution test are reported as estimated values.

10.3.7 **CAUTION:** If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

10.4 Continuing Calibration

10.4.1 Check calibration with an ICV following the initial calibration (Section 8.9). Verify calibration with the Continuing Calibration Verification (CCV) Standard (Section 8.9) at the end of the initial calibration sequence (ICV, ICB), after every ten samples, and at the

end of an analytical run. Use a calibration blank (Section 8.8.1) immediately following daily calibration, after every 10 samples and at the end of the analytical run.

10.4.1.1 The results of the ICV are to agree within 10% of the expected value, and CCVs are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument. Each may be rerun once to confirm or cure the initial failure.

10.4.1.2 The results of the calibration blank should be below ½ of LLOQ or RL (whichever is lower). If not, repeat the analysis and if the failure is repeated terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

10.4.2 Verify the inter-element and background correction factors at the beginning of each analytical run. Do this by analyzing the SIC (Section 8.10). Results must be less than +/- LLOQ for all non-spiked elements.

10.4.3 When low-level sensitivity is required, a check standard at the requested limit of quantitation is analyzed to confirm the reported detection limit (RDL). This is performed on a project-by-project basis.

10.5 Preventive Maintenance

Whenever instrument maintenance is performed, it is noted in the instrument's Maintenance Logbook.

10.5.1 Daily

Inspect the nebulizer pump tubing from the Autosampler to the Nebulizer. Replace if necessary.

10.5.2 Monthly or as needed

Remove the torch, "shot glass", nebulizer and spray chamber. Clean each with 10% Nitric Acid and rinse with tap water. Coat the inside of the spray chamber and shot glass with concentrated Sulfuric Acid and soak for one hour, then rinse well with DI water. Soak the torch and nebulizer in aqua regia overnight, then rinse with DI water.

10.5.3 Every 6 months

Preventive Maintenance is performed by the Vendor or in-house personnel as follows:

- check the cooling system
- flush/refill the chiller with distilled water and antibacterial conditioner
- clean the instrument to regain intensity
- clean/replace air filters.

11. Data Evaluation, Calculations and Reporting

11.1 If dilutions were performed, the appropriate factors must be applied to sample values. All results must be reported with up to three significant figures.

11.2 Soil samples

Soil samples are calculated as follows:

$$\mathbf{A} = \frac{\text{Sample weight (grams)}}{\text{Final Volume (mL)}}$$

$$\mathbf{B}\ (\text{concentration in mg/Kg}) = \frac{\text{Concentration of analyte (mg/L)}}{\mathbf{A}}$$

11.2.1 Dry weight correction

The LIMS calculates the dry weight correction, however it is calculated as follows:

$$\text{Final concentration in mg/Kg dry weight} = \frac{\mathbf{B}}{\%\ \text{Solids}}$$

11.3 Liquid samples

Liquid samples are calculated as follows:

$$\text{Dilution Factor} = \frac{\text{Final Volume (mL)}}{\text{Sample Volume (mL)}}$$

$$\text{Final concentration in mg/L} = \text{Concentration of analyte (mg/L)} \times \text{Dilution Factor}$$

11.4 Calculations for Hardness

The method for determining hardness is to compute it from the results of separate determinations of Calcium and Magnesium on aqueous samples.

11.4.1 Total Hardness

Total Hardness, mg equivalent $CaCO_3$/L = [2.497 (Ca, mg/L)] + [4.118 (Mg, mg/L)]

11.4.2 Calcium Hardness

Calcium Hardness, mg equivalent $CaCO_3$/L = [2.497 (Ca, mg/L)]

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

Also refer to Section 9 for Quality Control and acceptance criteria.

If the SIC is outside of the recovery window, then the standard is reanalyzed. If the standard failure continues, the IECs for the element/elements in question are reviewed and recalculated if necessary.

Immediate corrective action for a failing CCV/CCB includes reanalyzing the failing standard. If the standard passes the second time then the analysis may be continued. The raw data is noted. If the standard fails again, the problem must be found and corrected and the instrument is recalibrated. The ICV/ICB standard is reanalyzed and all previous data that had failed back to the previous passing CCV/CCB is reanalyzed.

The reanalysis procedure outline above is also conducted for a failing LCS or Method Blank; they may be rerun alone on the new or any subsequent passing bracket. The LCS or Method Blank do not qualify a bracket of samples but the batch run itself.

If the Matrix Spike does not meet acceptance criteria, a dilution test is performed. If the levels of the native sample is inadequate (see section 10.3.6) The RPD must be within 20% of the true value of the native sample. If the dilution test fails or the concentrations in the native sample are inadequate, the post spike is analyzed and evaluated (section 10.3.5). If these criteria are met, then the Matrix Spike data is reported, with the post spike narrated on the final report. If the post spike fails the data is reported as estimated.

If sample Duplicates are outside of the acceptance criteria, the analyst examines the sample for homogeneity. If the sample is not homogenous, this is narrated on the final report. Clean, homogenous samples are reanalyzed and if still outside of the acceptance limits, redigested and reanalyzed.

Sample nonconformance regarding a Matrix Spike recovery or a duplicate %RSD is narrated on the final report along with the corrective action(s) taken.

The mixed element SIC solution is analyzed at least once per day, immediately after the initial calibration. The concentration measured for any target analytes must be less than +/- the LLOQ. If this criterion is not met then sample analysis may not proceed until the problem is corrected, instrument is recalibrated, verified with the ICV/ICB and the SIC is then re-analyzed. Alternatively, the LLOQ may be raised to twice the concentration observed in the SIC solution if approved by the Department Manger or QA Department and the level is below the regulatory action limit or project specific requirements. The only exceptions are those elements that have been demonstrated to be contaminants in the SIC solutions These may be present up to the concentration documented plus the LLOQ. If failure continues notify the Department Supervisor or Manager.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05 unless supersede within this SOP. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP #1732 MDL/LOD/LOQ Generation

SOP# 1739 IDC/DOC Generation

SOP# 1728 Waste Management and Disposal

16. Attachments

TABLE 1: Element Wavelengths

TABLE 2: Precision and Accuracy Acceptance Criteria

TABLE 3: Reporting Limits

TABLE 1
ELEMENT WAVELENGTHS

Element	6500 Duo wavelength (nm)
Pb	220.3
Se	196.0
Sb	206.8
As	189.0
Ba	455.4
Be	313.0
Cd	214.4
Co	228.6
Cu	324.7
Cr	267.7
Fe	259.9
Mn	257.6
Mo	202.0
Ni	231.6
Ag	328.0
Tl	190.8
V	292.4
Zn	206.2
Al	396.1
Ca	315.8
Mg	279.0
B	208.9
Si	212.9
Sn	189.9
Sr	421.5
Ti	334.9
Bi	223.0
Na	589.5
K	766.4
S	180.7

TABLE 2
PRECISION AND ACCURACY ACCEPTANCE CRITERIA

	% Recovery LCS		Aqueous % Recovery MS		Soil % Recovery SRM *		Duplicate	
Element	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**	**Aqueous %RPD**	**Soil %RPD**
Aluminum	80	120	75	125	29	171	20	20
Antimony	80	120	75	125	4	196	20	20
Arsenic	80	120	75	125	81	119	20	20
Barium	80	120	75	125	83	118	20	20
Beryllium	80	120	75	125	83	117	20	20
Boron	80	120	75	125	70	129	20	20
Cadmium	80	120	75	125	82	117	20	20
Calcium	80	120	75	125	83	117	20	20
Chromium	80	120	75	125	80	119	20	20
Cobalt	80	120	75	125	83	117	20	20
Copper	80	120	75	125	83	117	20	20
Iron	80	120	75	125	51	150	20	20
Lead	80	120	75	125	80	120	20	20
Magnesium	80	120	75	125	74	126	20	20
Manganese	80	120	75	125	83	117	20	20
Molybdenum	80	120	75	125	81	119	20	20
Nickel	80	120	75	125	82	117	20	20
Potassium	80	120	75	125	74	126	20	20
Sulfur	80	120	75	125	NA	NA	20	20
Selenium	80	120	75	125	80	120	20	20
Silica (SiO_2)	80	120	75	125	NA	NA	20	20
Silver	80	120	75	125	66	134	20	20
Sodium	80	120	75	125	74	127	20	20
Strontium	80	120	75	125	80	120	20	20
Thallium	80	120	75	125	79	120	20	20
Tin	80	120	75	125	69	131	20	20
Titanium	80	120	75	125	82	118	20	20
Vanadium	80	120	75	125	79	121	20	20
Zinc	80	120	75	125	82	119	20	20

** Ranges of the SRM are presented as an example of a typical SRM; actual limits may vary by lot provided by the vendor.

TABLE 3
REPORTING LIMITS

Element	Aqueous (mg/L)	Soil (mg/Kg)
ALUMINUM	0.10	4.0
ANTIMONY	0.05	2.0
ARSENIC	0.005	0.40
BARIUM	0.01	0.40
BERYLLIUM	0.005	0.20
BORON	0.03	1.2
CADMIUM	0.005	0.40
CALCIUM	0.10	4.0
CHROMIUM	0.01	0.40
COBALT	0.02	0.80
COPPER	0.01	0.40
IRON	0.05	2.0
LEAD	0.01	2.0
MAGNESIUM	0.10	4.0
MANGANESE	0.01	0.40
MOLYBDENUM	0.05	2.0
NICKEL	0.025	1.0
POTASSIUM	2.5	100
SULFUR	0.25	10
SELENIUM	0.01	0.80
SILICA	0.50	20
SILVER	0.007	0.40
SODIUM	2.0	80
STRONTIUM	0.01	2.0
THALLIUM	0.02	0.80
TIN	0.05	4.0
TITANIUM	0.01	0.40
VANADIUM	0.01	0.40
ZINC	0.05	2.0

TABLE 4
LCS and Matrix Spike

Analyte	Liquid Concentration (mg/L)	Soil Concentration * (MS spike only) (mg/Kg)
Antimony	0.5	160
Arsenic	0.12	160
Barium	2.00	160
Beryllium	0.05	80
Cadmium	0.051	80
Chromium	0.20	160
Copper	0.25	160
Lead	0.51	160
Nickel	0.50	160
Selenium	0.12	160
Silver	0.05	40
Thallium	0.12	160
Zinc	0.50	160
Iron	1.00	800
Manganese	0.50	160
Calcium	10.0	800
Magnesium	10.0	800
Potassium	10.0	800
Sodium	10.0	800
Silica	1.0	800
Aluminum	2.00	800
Cobalt	0.50	160
Vanadium	0.50	160
Boron	1.0	NA
Molybdenum	1.0	NA
Titanium	1.0	NA

*MS spike of a solid based on 1.25g and a final volume of 50 mL.

Note: Solids LCS is an SRM with certified value provided by the vendor on a lot basis.

PCBs

By Capillary Column Gas Chromatography

Reference Methods: Method 8082A SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update IV, 2007.

Quality Control Requirements and Performance Standards for Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography (GC) in Support of Response Action under the Massachusetts Contingency Plan (MCP), Revision No.1, July 1, 2010.

State of Connecticut, Department of Environmental Protection, RRCP, Version 2.0, July 2006.

1. Scope and Application

Method 8082A is used to determine the concentrations of Polychlorinated Biphenyls (PCBs) as Aroclors in extracts from solid and liquid matrices. This SOP details the analysis for PCBs using fused-silica, open-tubular, capillary columns with electron capture detectors (ECD).
Matrices: Extracts from solid and liquid matrices.

Definitions: See Alpha Laboratories Quality Manual Appendix A

Regulatory Parameter List: The standard compounds listed below are determined by this method.

Parameter	CAS#
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5
Aroclor 1262	37324-23-5
Aroclor 1268	11100-14-4

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.
This method is restricted to use by or under the supervision of analysts experienced in the operation of the gas chromatograph (GC) and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability (see section 13.2).

2. Summary of Method

A measured volume or weight of sample (volumes and weights can vary but approximately 1L or 125 mls (LVI – Low Volume Initiative) for liquids, 15g to 30g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

Liquid samples are extracted at neutral pH with methylene chloride using Method 3510C (separatory funnel), or other appropriate technique. See extraction SOP for details.

Solid samples are extracted with methylene chloride: acetone (1:1) using Method 3540C (Soxhlet), or other appropriate technique. Solid samples may also be extracted with hexane:acetone (1:1) using Method 3546 (microwave). See extraction SOP for details.

Wipe samples are extracted with methylene chloride: acetone (1:1) using Method 3540C (Soxhlet) or other appropriate technique. See extraction SOP for details.

Oil samples are diluted with hexane following the procedure outlined in the extraction SOP.

Sulfuric acid cleanup (Method 3665A), Copper cleanup (Method 3660B) and Silica Gel cleanup (Method 3630) are utilized for PCB extracts. See extraction SOP for details.

After cleanup, the extract is analyzed by injecting 1µL into a gas chromatograph equipped with narrow- or wide-bore fused silica capillary columns and electron capture (GC/ECD) detectors.

2.1 Method Modifications from Reference

Not applicable.

3. Reporting Limits

The reporting limits for this method as outlined is as follows:

- Aqueous samples: 0.25 ug/L / Aroclor (based on a 1L extraction or 125 ml LVI extraction)
- Soil Samples: 33.3 ug/kg / Aroclor (based on a 15g extraction)
- Solid of Difficult Matrices (i.e Caulking, Concrete, etc. are logged using the Alpha Low Level 8082 products): based on a 15g extraction
    - Aroclors 1016, 1221, 1232, 1242, 1254: 20 ug/kg
    - Aroclors 1248, 1260: 13.3 ug/kg
    - Aroclors 1262, 1268: 6.67 ug/kg

4. Interferences

4.1 Instrumental

4.1.1 Only high purity gases are used in the GC system to eliminate this source of possible contamination. Both the helium (carrier gas – 99.999%) and argon-methane (detector make-up gas) are certified by the gas supplier.

4.1.2 Preventive instrument maintenance is performed routinely, and whenever highly contaminated extracts are analyzed that could result in chromatographic interferences or result in degradation of system performance. Section 10.5 details the maintenance steps.

4.1.3 Glassware must be scrupulously cleaned. This procedure is detailed in the Organic Extraction Cleaning and Handling SOP/1953. Store dry glassware in a clean environment.

4.2 Parameters

4.2.1 All solvents used are pesticide grade or equivalent, and reagents are purchased as certified contaminant free. All of these materials are routinely determined to be free of interferences by analysis of extraction blanks with every extraction batch performed.

4.2.2 Certain compounds (i.e. phthalates) can be extracted from the sample matrix and be detected by the ECD that could possibly result in false positive results or complicate the data interpretation. The use of the cleanup procedures detailed in the extraction SOP minimizes these possible interferences. Analyst experience is also crucial in making compound determinations.

4.2.3 Interferences co-extracted from the samples will vary considerably from waste to waste. While a general cleanup technique is referenced or provided as part of the method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. PCBs have been tentatively classified as known or suspected human or mammalian carcinogens. Additional references to laboratory safety are available in the Chemical Hygiene Plan.
All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.1 Lab coats, safety glasses, and gloves must be worn when handling samples, extracts, standards or solvents.

5.2 All solvent and extract transfers must be handled in the vented bench area in the GC laboratory.

5.3 All stock standards, working standards, and vialed sample extracts must be placed into the waste bucket in the lab, for future disposal by the Hazardous Waste Manager. The container must be labeled properly with hazard warning labels indicating the container contents.

5.4 Bottles containing flammable solvents must be stored in the flammables cabinet.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Aqueous samples are collected in two 1L or two 125 ml (LVI) amber glass jars with teflon-lined lids. Solid samples are collected in one 250 mL wide-mouth glass jar with a teflon-lined lid. All containers are purchased pre-cleaned and certified from commercial vendors.

6.2 Sample Preservation

Both aqueous and solid samples are then preserved by packing in coolers with ice or ice packs, to maintain a temperature of 4 ± 2° C. Upon receipt at the laboratory, the samples are transferred into sample storage refrigerators to maintain at a temperature of 4 ± 2° C.

6.3 Sample Handling

Aqueous samples must be extracted within 7 days of sample collection, solid samples within 14 days of collection. Once extracted, the samples must be analyzed within 40 days of the extraction date.

7. Equipment and Supplies

7.1 Gas Chromatograph, Agilent 6890, 7890: An analytical system complete with gas chromatograph configured for split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and data system.

7.2 GC Columns: Alpha utilizes dual-column analyses. The dual-column approach involves either a single injection that is split between two columns that are mounted in a single gas chromatograph. Typical column pair used is listed below. Other columns may be used as long as method performance criteria can be met.

Column pair:

RTX-CLP: Cat. #11141 from Restek or equivalent; 30m, 0.32mm, 0.32µm

RTX-CLPII Cat. #11324 from Restek or equivalent; 30m, 0.32mm, 0.25µm

7.3 Guard Column: Cat. #10027 from Restek or equivalent; 5m, 0.32mm

7.4 Class "A" Volumetric Flasks: 10mL and 25mL (and other volumes), for standards preparation

7.5 Microsyringes/Wiretrol syringes: 10 µL – 1000 µL

7.6 Gooseneck splitless injecton liner, Cat #20799-214.5 from Restek or equivalent

7.7 Universal "Y" Press-tight tee split: Cat. #20406 from Restek or equivalent / **Siltek MXT Connector:** Cat. #21388 from Restek or equivalent

8. Reagents and Standards

Reagent grade or pesticide grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.
NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4 ± 2° C in Teflon(R)-sealed containers in the dark. When a Lot of standards is prepared, aliquots of that Lot are stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC tests indicate a problem. All other standard solutions must be replaced after six months or sooner if routine QC indicates a problem.

8.1 n-Hexane: Pesticide quality or equivalent.

8.2 Acetone: Pesticide quality or equivalent.

8.3 Organic-free Reagent Water: All references to water in this method refer to organic-free reagent water from Alpha's RO water treatment system.

8.4 Stock Standard Solutions: All stock standard solutions are purchased from commercial vendors as ampulated certified solutions. When an ampulated stock solution is opened, it is transferred to a labeled amber screw-cap vial. The expiration date of the stock solution is either the vendor specified expiration date, or 1 year from the date the ampule was opened, whichever is sooner.

8.5 Calibration Standards: Calibration standards are prepared volumetrically by diluting the appropriate stock standard(s) with hexane. Calibration standards expire 6 months from the date of preparation, or on the earliest expiration date of any of the stock solutions used to prepare the calibration standard. Calibrations are performed at the 6 concentration levels listed in Table 1. The list of ampulated calibration standards are obtain from **Ultra**:

- Aroclor 1016, Cat. #PP-282, at 100ug/ml
- Aroclor 1260, Cat. #PP-361, at 100ug/ml
- Aroclor 1262, Cat. #PP-371, at 100ug/ml
- Aroclor 1268, Cat. #PP-382, at 100ug/ml
- Aroclor 1221, Cat. #PP-292, at 100ug/ml
- Aroclor 1232, Cat. #PP-302, at 100ug/ml
- Aroclor 1242, Cat. #PP-312, at 100ug/ml
- Aroclor 1248, Cat. #PP-342, at 100ug/ml
- Aroclor 1254, Cat. #PP-351, at 100ug/ml

8.6 Second Source Standards: (ICV/CCAL) Continuing Calibration standards are prepared volumetrically by diluting the appropriate stock standard(s) with hexane. Continuing Calibration standards expire 6 months from the date of preparation, or on the earliest expiration date of any of the stock solutions used to prepare the standard. The list of ampulated standards are obtain from **Accustandard**:

- Aroclor 1016, Cat. #C-216S-H-10X, at 1000ug/ml
- Aroclor 1260, Cat. #C-260S-H-10X, at 1000ug/ml
- Aroclor 1262, Cat. #C-262S-H-10X, at 1000ug/ml
- Aroclor 1268, Cat. #C-268S-H-10X, at 1000ug/ml
- Aroclor 1221, Cat. #C-221S-H-10X, at 1000ug/ml
- Aroclor 1232, Cat. #C-232S-H-10X, at 1000ug/ml
- Aroclor 1242, Cat. #C-242S-H-10X, at 1000ug/ml
- Aroclor 1248, Cat. #C-248S-H-10X, at 1000ug/ml
- Aroclor 1254, Cat. #C-254S-H-10X, at 1000ug/ml

8.7 Internal Standard Solution: 1-Bromo-2-nitrobenzene (Ultra, Cat. #PPS-351) is used as the internal standard, and is added to all single-component calibration standards and sample extracts to achieve a concentration of 0.25µg/mL. For LVI, this solution is diluted 10X more, achieving a concentration of 0.025µg/mL.

8.8 Surrogate Standards: Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB) are used as surrogates for Aroclor analysis. They are added to the calibration standards at the concentrations listed in Table 1, Continuing Calibration Standards and are spiked into all samples and QC samples prior to extraction.

- **ICAL Surrogates Stock:** is prepared by diluting of 500ul of Pesticides Surrogates Standard Spiking Solution (Ultra, Cat. #ISM-320-1) and 500ul of Decachlorobiphenyl (Accustandard, Cat. #CLP-032-R-01) to 20ml of Hexane to achieve concentration of TCMX at 5ug/ml and DCB at 10ug/ml. For LVI, this solution is diluted 10X more, achieving a concentration of 0.5 ug/ml for TCMX and 0.1 ug/ml for DCB.
- **CCAL Surrogates Stock:** is prepared by diluting of 1ml of TCMX&DCB (Accustandard, Cat. #CLP-032-R) and 1ml of Decachlorobiphenyl (Accustandard, Cat. #CLP-032-R-01) to 20ml of Hexane to achieve concentration of TCMX at 10ug/ml and DCB at 20ug/ml. For LVI, this solution is diluted 10X more, achieving a concentration of 1 ug/ml for TCMX and 2 ug/ml for DCB.
- **Extraction Surrogates Stock:** is prepared by diluting of 10ml of TCMX&DCB (Accustandard, Cat. #CLP-032-R) to 1000ml of Acetone to achieve concentration of TCMX and DCB at 2ug/ml. For LVI, this solution is diluted 10X more, achieving a concentration of 0.2 ug/ml for both TCMX and DCB.

8.9 LCS/MS Spiking Solutions: The LCS/MS spiking solution is prepared by diluting of 6.25ml of Arochlor 1016/1260 (Restek, Cat. #32039) to 500ml of Acetone to achieve concentration of Arochlor 1016/1260 at 12.5ug/ml. For LVI, 1.25 ml of the stock solution is diluted to 500 mls of Acetone to achieve a concentration of Aroclor 1016/1260 at 2.5 ug/ml.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

A Method Blank is an aliquot of a clean reference matrix (reagent water for water samples or Ottawa sand for soil/sediment samples) that is carried through the entire analytical procedure. Extraction blanks are performed with each extraction batch of 20 or less samples, according to the extraction SOPs. The extraction blank must not contain any of the reportable analytes above the reporting limit. If any reportable analytes are detected in the blank, the entire extraction batch is suspect and re-extraction of all associated samples is required, unless the associated samples are non-detect or concentration of the analyte in the samples is 10 times greater than the concentration of this analyte in the blank. The surrogate recoveries must also be within the acceptance criteria listed in Table 2. If surrogate acceptance criteria are exceeded, the extraction batch must be evaluated to determine if re-extraction or re-analysis is necessary.

9.2 Laboratory Control Sample (LCS)

A Laboratory Control Sample (LCS)/ Laboratory Control Sample Duplicate (LCSD) pair is extracted with each analytical batch. The LCS/LCSD consist of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. For Aroclor analysis, the LCS/LCSD are spiked with a mixture of Aroclor 1016 and 1260. The recovery acceptance criteria are listed in Table 2. If any recovery criteria are not met, the extract may be re-analyzed. If the criteria are still not met, the **entire batch is re-extracted**, unless the recoveries are high and the associated samples are non-detect. If this is not possible, due to insufficient sample or holding time exceedances, the analyst must narrate the failure in the LIMS for inclusion in the client report.

9.3 Initial Calibration Verification (ICV)

Refer to Section 10.2.7.

9.4 Continuing Calibration Verification (CCV)

Refer to Section 10.4.

9.5 Matrix Spike

Upon client request, a matrix spike and matrix spike duplicate pair are extracted and analyzed with each batch of 20 or less samples. The MS/MSD pair is extracted and analyzed for standard PCB analysis. The recovery acceptance criteria are listed in Table 2. If the recovery criteria are not met, but are met in the LCS, the failure may be attributed to sample matrix effects and must be narrated for inclusion in the client report.

9.6 Laboratory Duplicate

Upon client request, a Laboratory Duplicate is extracted and analyzed with each batch of 20 or less samples. The relative percent difference (RPD) acceptance criteria are listed in Table 2. If the RPD criteria are not met, the failure may be attributed to matrix effect and must be narrated for inclusion in the client report.

9.7 Surrogates

All extracted samples and associated QC are spiked with Extraction Surrogates Stock to achieve concentration of TCMX and DCB at 0.5ug/ml (0.2 ug/ml for LVI). The laboratory must evaluate surrogate recovery data from individual samples and QC samples versus the surrogate control limits listed in Table 2. If the surrogate limits are not met, the extract may be reanalyzed to determine if the failure was due to an instrument problem. If the criteria are still not met, the affected samples must be re-extracted to confirm that the failure was due to sample matrix, unless the surrogate recovery is high and the associated sample is non-detect. If matrix effect is confirmed, this must be noted on a narrative sheet for inclusion in the client report.

9.8 Method Sequence

Typical Initial calibration (each level to identified with the standard lot number)

1. Prime
2. Blank
3. Standard Level 1
4. Standard Level 2
5. Standard Level 3

6. Standard Level 4
7. Standard Level 5
8. Standard Level 6
9. Initial Calibration Verification Standard (ICV)

Repeat steps 3 – 9 as needed for each Aroclor necessary for calibration.

NOTE: If multiple calibration mixtures are analyzed, it is acceptable to analyze appropriate ICVs after all calibration standards have been injected.

Typical Daily Sequence

1. 1016/1260 Continuing Calibration Standard **(identified with the standard lot number)**
2. Extraction Blank
3. Laboratory Control Sample
4. Matrix Spike / Matrix Spike Duplicate (if requested by Client)
5. Duplicate (if included with batch QC)
6. Samples up to 16
7. Repeat 1 – 6 as needed.

10. Procedure

10.1 Equipment Set-up

10.1.1 GC Conditions:

The dual-column / dual-detector approach involves the use of the columns listed in section 7.2. The columns are connected to an injection tee or dual injection GC, and separate electron capture detectors. Alpha typical GC conditions are listed below, but may be altered as long as method performance criteria are met.

Temperature1: 120 ºC	Injector temerature: 250ºC
Time1: 0 minutes	Injector mode: Pulsed Split
Ramp1: 45ºC/minute	1.4:1 split, 0.20 min pulse
Temperature2: 200ºC	Injector Flow: 5.7 ml/min split flow
Time2: 0 minutes	Detector temperature: 350ºC
Ramp2: 15ºC/minute	Carrier gas: Helium
Temperature3: 230ºC	Carrier flow: 20ml/min
Time3: 0 minutes	Carrier mode: Constant flow
Ramp3: 30ºC/minute	Makeup gas: Argon/methane (P5)
Final temperature 330ºC	Total detector flow: 55ml/min
Final time: 2 minutes	Injection Volume: 1 µL

10.2 Initial Calibration

10.2.1 Prepare calibration standards using the standards listed in Section 8.5 to achieve the concentrations from Table 1. Alternatively, a standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing multi-point initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. Single standards of each of the other seven Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards have been used to demonstrate the linearity of the detector, these single standards of the remaining seven Aroclors also may be used to determine the calibration factor for each Aroclor when a linear calibration model through the origin is chosen. Prepare a standard for each of the other Aroclors. The concentrations should generally correspond to the mid-point of the linear range of the detector, but lower concentrations may be employed.

10.2.2 Establish the GC operating conditions by loading the appropriate GC method. Typical instrument conditions are listed in section 10.1.1. The same operating conditions are used for calibrations and sample analyses. Create the analytical sequence using the Agilent Chemstation data acquisition software. Record the calibration standard, unique lot number (PP#) and analyst's initials in the analytical sequence list.

10.2.3 A 1µL injection volume of each calibration standard is typically used. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest. The same injection volume must be used for all standards and samples.

10.2.4 Column adsorption may be a problem when the GC has not been used for a day or more or after system maintenance. The GC column may be primed (or deactivated) by injecting a PCB standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

Alternately, the system may be primed by baking at the final analytical temperature for approximately 30 minutes.

Several analytes may be observed in the injection just following system priming. Always run an instrument blank after system priming.

10.2.5 **Calibration Factor:** Internal standard calibration techniques are employed in this method.

10.2.5.1 Internal Standard Procedure. In each standard, calculate the response factor (RF) for each analyte, the average RF, and the relative standard deviation (RSD) of the RFs, using the Enviroquant data processing software. The calculations are performed automatically, using the formula listed in Alpha's Quality Manual.

Alternatively, standards of the other seven Aroclors are necessary for pattern recognition. When employing the traditional model of a linear calibration through the origin, these standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 mixture has been

used to describe the detector response. The standards for these seven Aroclors should be analyzed before the analysis of any samples with hits above the RL. For example, an Aroclor 1254 standard should be analyzed before a sample with a hit of Aroclor 1254.

10.2.6 Initial Calibration Criteria

- If the **RSD for an analyte is < 20%**, then the response of the instrument for this compound is considered linear over the range and the mean calibration factor can be used to quantitate sample results.
- If the **RSD for any analyte is > 20%**, then linearity through the origin cannot be assumed. The mean response factor cannot be used for quantitation. An alternative calculation may be done by the use of **linear regression** or **quadratic regression** (minimum of six ICAL points are needed and regression must be weighted inversely proportional to concentration) as long as the correlation coefficient is **>0.990**. If both of these quantitation methods fail criteria for any compound in the initial calibration, then the system must be reevaluated and a new calibration curve must be analyzed. If quadratic regression is used for calibration, this must be noted in the laboratory narrative.
- **MCP requirement**: minimum of five unique peaks must be evaluated for Aroclors 1016 and 1260.
- **MCP requirement:** If linear or non-linear regression is used, RL must to be verified by recalculating concentrations in the lowest calibration standard using the final calibration curve. Recoveries must be **70-130%.**
- **MCP requirement:** Minimum of five standards (or six if non-linear regression used) must be used.

Initial Calibration Verification

An initial calibration verification standard must be run immediately after each initial calibration, near the midpoint of the curve. The standard must be prepared using a second source that is different than the source used for the initial calibration. (Standards listed in Section 8.6). The **%D** has to be within **20%** (**15% for CT RCP**) when compared to the mean response factor from the initial calibration.

10.2.7 Retention Time Window

10.2.7.1 The retention time window used for the identification of target analytes is ± 0.07 minutes. These criteria have been adopted from the EPA CLP Statement of Work (OLM04.2). It has been found that these limits work well, being wide enough to eliminate false-negatives while being tight enough to eliminate false-positives. Windows that are calculated using the procedure recommended in Method 8000 tend to be very narrow, creating the risk of false negative results.

10.2.7.2 The windows listed above are used as guidance; however the experience of the analyst weighs heavily in the interpretation of the chromatograms. For example, it has been observed that certain oil matrices can cause the retention times to shift more dramatically.

10.3 Sample Processing

The determination of PCB Aroclors is accomplished by comparing the sample chromatogram to that of the most similar Aroclor standard. The use of PCB overlays is extremely helpful, either by using hardcopies of chromatograms or by utilizing the Enviroquant software. A choice must be made as to which Aroclor is most similar and whether that standard is truly representative of the PCB in the sample. Both retention time and pattern are important when determining PCBs in a sample.

Samples that contained weathered PCB present special analytical challenges. Weathering could alter the Aroclor pattern to the extent that different peaks have to be selected for quantitation. Samples that contained more than one Aroclor present similar problems. For these samples, the Analyst may have to consider selecting the earlier eluting peaks for the lower boiling Aroclor and selecting the later eluting peaks for the higher boiling Aroclors to minimize overlapping peaks. Minimum of 3 peaks must be chosen for each Aroclor. In these instances, the Analyst may need request the assistance of someone with more expertise in determining the presence of PCB Aroclor.

If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract may be needed. If instrument problems are suspected, rerun the extract on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to the extraction SOPs for the procedures to be followed in sample cleanup.

The laboratory must report the ***HIGHER*** of the two results unless obvious interference is present on of the columns.

10.4 Continuing Calibration

10.4.1 Verify calibration each **12-hours** shift by injecting calibration verification standards prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than **once every twenty injections**. A bracketing CCV is not required with the use of internal standard calibration (Method 8082A 11.6.8) with the exception of samples ran under CT RCP method. For Aroclor analysis, the calibration verification standard should be a mixture of Aroclor 1016 and 1260. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition (Method 8082A 11.6.2). However, if the one-point calibration is used for the seven other Aroclor, a calibration standard must be analyzed before the sample for any hits.

10.4.2 The response factor (for internal standard compounds) for each analyte to be quantitated must not exceed a **± 20% difference** when compared to the initial calibration curve (**± 15% for CT RCP**). The Target data processing software automatically calculates the %D for all analytes according to the formulae in Alpha's Quality Manual. A retention time shift >30 seconds for the internal standard necessitates reanalysis of all affected samples.

10.5 Internal Standard

The use of internal standard calibration does not require that all sample results be bracketed with CCV standard. However, when internal standard calibration is used, the

retention times of internal standards and the area response of internal standards should be checked for each analysis.

10.5.1 **IS in CCAL** – The measured area of the internal standard must be no more than ± 50% different from the average area calculated during initial calibration **(-50 to 150%).**

10.5.2 **IS in samples** - The measured area of the internal standard must be no more than -50% to +100% different from the area calculated from opening CCV **(-50 to 200%)**

Retention time shifts of more than 30 sec from the retention time of the most recent calibration standard are cause for concern and must be investigated.

10.6 Preventive Maintenance

10.6.1 **Preventive Maintenance:** Routine preventive maintenance is performed to maintain GC system performance. This includes periodic replacement of injector septa, replacement of injector liner(s), and replacement of injector seals.

10.6.2 **Other Maintenance:** ECD detectors may become contaminated, requiring bake out at elevated temperatures, (no greater than 375°C) or repair by the manufacturer.

11. Data Evaluation, Calculations and Reporting

11.1 Quantitation of Aroclors

Per Method 8082A, quantitation is based on the use of a minimum of 3 of the major peaks present in the analyte, although the use of 5 of the major peaks is recommended. Each of these peaks is individually calibrated with a **minimum of five calibration points** based on average response factors. The %RSD must meet the criteria of ≤20% for the ICAL. The five major peaks are calculated as described below. After individual calculation meets criteria, the average of the peaks selected for quantitation is used to determine the final concentration.

11.1.1 Aqueous samples

$$\text{Concentration } (\mu g/L) = \frac{C \times DF \times Vf \times 1000}{Vo}$$

where:

C = Extract concentration (µg/mL), **NOTE**: ng on column = ng/injection volume = ng/uL = ug/mL

DF = Dilution factor

Vf = Final extract volume (mL)
Vo = Sample volume (mL)

11.1.2 Soil/sediment samples

$$\text{Concentration (µg/Kg, dry weight)} = \frac{C \times DF \times Vf \times 1000}{W\ (gm)} \div \%S$$

where:
C = Extract concentration (µg/mL), **NOTE**: ng on column = ng/injection volume = ng/uL = ug/mL
DF = Dilution factor
Vf = Final extract volume (mL)
W = Weight of the sample extracted (10g for high, 30g for low)
%S = Percent solids, as a decimal value

11.1.3 Reporting Results

11.1.3.1 After performing technical data review, validating that all QC criteria have been met and confirming all positive hits, the data report is sent electronically to the LIMS computer for generation of the client report. There are two levels of review of the data in the LIMS system prior to release of data. These reviews must be done by two separate individuals.

11.1.3.2 Reporting Results for PCBs in Caulk Samples

If in the screen sample Aroclor concentration as calculated above is **> 20000ppm**, the Client is contacted by a Customer Service Representative and these results are sent to the LIMS and reported to the Client.

If the sample concentration as calculated above for any Aroclor is **< 20000ppm**, the sample is sent for re-extraction by Method 3540C (Alpha SOP/1954).

11.1.3.3 Summation Rules

"TOTAL" concentrations are calculated for **ALL samples and Quality Control Samples** (i.e. LCS, MS, DUP, BLK).

TOTAL = sum of "reportable" Aroclors

Reportable- all Aroclors reported for associated project.

For dual-column analysis, Total is reported as part of column "A" data, unless all individuals are reported from "B" column. "Total" is calculated based on the associated "Report List". See Work Instruction #14335 for details.

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

Holding time exceedance and/or improper preservation are noted on the nonconformance report form.

Perform instrument maintenance as described throughout this SOP as needed when instrument calibration criteria are not met. Record all maintenance in the instrument logbook.

All batch and sample specific QC criteria outlined in Section 10 are evaluated by the analyst prior to approval of the data. When any QC criteria fail, the cause for the failure must be identified and corrected. This may include instrument recalibration followed by sample reanalysis, sample cleanup, or sample re-extraction. If it is determined that the failure is due to sample matrix effects, a project narrative report is written into the LIMS by the analyst for inclusion in the data report. If there is insufficient sample volume to perform the re-analysis for confirmation, this is also noted in the narrative and included in the client report.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/1732 MDL/LOD/LOQ Generation

SOP/1739 IDC/DOC Generation

SOP/1728 Waste Management and Disposal SOP

16. Attachments

Table 1: STANDARD SOLUTIONS

Table 2: QC ACCEPTANCE CRITERIA

TABLE 1

STANDARD SOLUTIONS – Suggested Concentrations

STANDARD SOLUTIONS	Stock solution (ug/mL)	Level 1 (ug/mL)	Level 2 (ug/mL)	Level 3 (ug/mL)	Level 4 (ug/mL)	Level 5 (ug/mL)	Level 6 (ug/mL)	Spike Solution (ug/mL)	LCS Solution (ug/mL)
PCB									
Aroclor 1016/1260	100	0.1	0.5	1	2.5	5	10	12.5	12.5
Aroclors 1221, 1232, 1242, 1254, 1262, 1268	100	0.1	0.5	1	2.5	5	10		
LVI		0.01	0.05	0.1	0.25	0.5	1	2.5	2.5
Internal Standard									
1-Bromo-2-Nitrobenzene	5000	0.25	0.25	0.25	0.25	0.25	0.25		
LVI		0.025	0.025	0.025	0.025	0.025	0.025		
Surrogates:									
Tetrachloro-m-xylene	2.0	0.0064	0.032	0.064	0.16	0.32	0.64	2	2
Decachlorobiphenyl	2.0	0.0126	0.064	0.128	0.32	0.64	1.28	2	2
LVI – 10X less								0.2	0.2

LVI is spiked 10X lower

TABLE 2

QC ACCEPTANCE CRITERIA

	Aqueous, Soils	
Surrogate % Recovery	**Lower Control Limit**	**Upper Control Limit**
2,4,5,6-Tetrachloro-m-xylene	30%	150%
Decachlorobiphenyl	30%	150%

	Aqueous, Soils % Recovery		Duplicate and/or MSD	
MS/MSD and LCS	**Lower Control Limit**	**Upper Control Limit**	**Aqueous RPD**	**Soil RPD**
Aroclor 1016, 1260	40%	140%	30%	50%

Determination of Selected Perfluorinated Alkyl Substances in Non-Potable Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

Reference: EPA Method 537, Version 1.1, September 2009, EPA Document #: EPA/600/R-08/092

EPA Method 537.1, Version 1, November 2018, EPA Document #: EPA/600/R-18/352

Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.2, 2018

1. Scope and Application

Matrices: Non-potable water

Definitions: Refer to Alpha Analytical Quality Manual.

1.1 This is a liquid chromatography/tandem mass spectrometry (LC/MS/MS) method for the determination of selected perfluorinated alkyl substances (PFASs) in Non-potable Water. Accuracy and precision data have been generated in reagent water, and finished ground and surface waters for the compounds listed in Table 1.

1.2 The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the operation of the LC/MS/MS and in the interpretation of LC/MS/MS data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

Table 1

Parameter	Acronym	CAS
Hexafluoropropylene oxide dimer acid [1]	HFPO-DA	13252-13-6
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluorodecanoic acid	PFDA	335-76-2
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorohexanesulfonic acid	PFHxS	355-46-4
Perfluorohexanoic acid	PFHxA	307-24-4

Table 1 (cont.)

Perfluorononanoic acid	PFNA	375-95-1
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorotetradecanoic acid	PFTA	376-06-7
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluoroundecanoic acid	PFUnA	2058-94-8
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4

2. Summary of Method

2.1 A 250-mL water sample is fortified with surrogates and passed through a solid phase extraction (SPE) cartridge containing polystyrenedivinylbenzene (SDVB) to extract the method analytes and surrogates. The compounds are eluted from the solid phase with a small amount of methanol. The extract is concentrated to dryness with nitrogen in a heated water bath, and then adjusted to a 1-mL volume with 96:4% (vol/vol) methanol: water after adding the IS(s). A 3µL injection is made into an LC equipped with a C18 column that is interfaced to an MS/MS. The analytes are separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the internal standard technique. Surrogate analytes are added to all Field and QC Samples to monitor the extraction efficiency of the method analytes.

2.2 Method Modifications from Reference

2.2.1 None.

3. Reporting Limits

3.1 The reporting limit for PFAS's is 2 ng/L (4ng/L for HFPO-DA).

4. Interferences

4.1 PFAS standards, extracts and samples should not come in contact with any glass containers or pipettes as these analytes can potentially adsorb to glass surfaces. PFAS analyte, IS and SUR standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in polypropylene containers.

4.2 Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample bottles and caps, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. The method analytes in this method can also be found in many common laboratory supplies and equipment, such

as PTFE (polytetrafluoroethylene) products, LC solvent lines, methanol, aluminum foil, SPE sample transfer lines, etc. All items such as these must be routinely demonstrated to be free from interferences (less than 1/3 the RL for each method analyte) under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 9.2. **Subtracting blank values from sample results is not permitted.**

4.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water. Humic and/or fulvic material can be co-extracted during SPE and high levels can cause enhancement and/or suppression in the electrospray ionization source or low recoveries on the SPE sorbent. Total organic carbon (TOC) is a good indicator of humic content of the sample. Under the LC conditions used during method development, matrix effects due to total organic carbon (TOC) were not observed.

4.4 Relatively large quantities of the preservative (Sect. 6.2.1) are added to sample bottles. The potential exists for trace-level organic contaminants in these reagents. Interferences from these sources should be monitored by analysis of laboratory reagent blanks (Sect. 9.2.1), particularly when new lots of reagents are acquired.

4.5 SPE cartridges can be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and lots of SPE devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

5. Health and Safety

5.1 The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

5.2 All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.3 PFOA has been described as “likely to be carcinogenic to humans.” Pure standard materials and stock standard solutions of these method analytes should be handled with suitable protection to skin and eyes, and care should be taken not to breathe the vapors or ingest the materials.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

6.1.1 Samples must be collected in three (3) 250-mL high density polyethylene (HDPE) container with an unlined plastic screw cap.

6.1.2 The sample handler must wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. PFAS contamination during sampling can occur from a number of common sources, such as food packaging

and certain foods and beverages. Proper hand washing and wearing nitrile gloves will aid in minimizing this type of accidental contamination of the samples.

6.1.3 Open the tap and allow the system to flush until the water temperature has stabilized (approximately 3 to 5 min). Collect samples from the flowing system.

6.1.4 Fill sample bottles, taking care not to flush out the sample preservation reagent. Samples do not need to be collected headspace free.

6.1.5 After collecting the sample, cap the bottle and agitate by hand until preservative is dissolved. Keep the sample sealed from time of collection until extraction.

6.1.6 Field Reagent Blank (FRB)

6.1.6.1 A FRB must be handled along with each sample set. The sample set is composed of samples collected from the same sample site and at the same time. At the laboratory, fill the field blank sample bottle with reagent water and preservatives, seal, and ship to the sampling site along with the sample bottles. For each FRB shipped, an empty sample bottle (no preservatives) must also be shipped. At the sampling site, the sampler must open the shipped FRB and pour the preserved reagent water into the empty shipped sample bottle, seal and label this bottle as the FRB. The FRB is shipped back to the laboratory along with the samples and analyzed to ensure that PFASs were not introduced into the sample during sample collection/handling.

6.1.6.2 The same batch of preservative must be used for the FRBs as for the field samples.

6.1.6.3 The reagent water used for the FRBs must be initially analyzed for method analytes as a MB and must meet the MB criteria in Section 9.2.1 prior to use. This requirement will ensure samples are not being discarded due to contaminated reagent water rather than contamination during sampling.

6.2 Sample Preservation

6.2.1 The preservation reagent, listed in the table below, is added to each sample bottle as a solid prior to shipment to the field (or prior to sample collection).

Table 2

Compound	Amount	Purpose
Trizma	5.0 g/l	Buffering reagent and removes free chlorine

6.3 Sample Shipping

6.3.1 Samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Sample temperature must be confirmed to be at or below 10 °C when the samples are received at the laboratory. Samples stored in the lab must be held at or below 6 °C until extraction, but should not be frozen.

NOTE: Samples that are significantly above 10° C, at the time of collection, may need to be iced or refrigerated for a period of time, in order to chill them prior to shipping. This will allow them to be shipped with sufficient ice to meet the above requirements.

6.4 Sample Handling

6.4.1 Holding Times

6.4.1.1 Water samples should be extracted as soon as possible but must be extracted within 14 days. Extracts must be stored at room temperature and analyzed within 28 days after extraction.

7. Equipment and Supplies

7.1 SAMPLE CONTAINERS – 250-mL high density polyethylene (HDPE) bottles fitted with unlined screw caps. Sample bottles must be discarded after use.

7.2 POLYPROPYLENE BOTTLES – 4-mL narrow-mouth polypropylene bottles.

7.3 CENTRIFUGE TUBES – 15-mL conical polypropylene tubes with polypropylene screw caps for storing standard solutions and for collection of the extracts.

7.4 AUTOSAMPLER VIALS – Polypropylene 0.7-mL autosampler vials with polypropylene caps.

7.4.1 NOTE: Polypropylene vials and caps are necessary to prevent contamination of the sample from PTFE coated septa. However, polypropylene caps do not reseal, so evaporation occurs after injection. Thus, multiple injections from the same vial are not possible.

7.5 POLYPROPYLENE GRADUATED CYLINDERS – Suggested sizes include 25, 50, 100 and 1000-mL cylinders.

7.6 MICRO SYRINGES – Suggested sizes include 5, 10, 25, 50, 100, 250, 500 and 1000-µL syringes.

7.7 PLASTIC PIPETS – Polypropylene or polyethylene disposable pipets.

7.8 ANALYTICAL BALANCE – Capable of weighing to the nearest 0.0001 g.

7.9 SOLID PHASE EXTRACTION (SPE) APPARATUS FOR USING CARTRIDGES

7.9.1 SPE CARTRIDGES – 0.5 g, 6-mL SPE cartridges containing styrenedivinylbenzene (SDVB) sorbent phase.

7.9.2 VACUUM EXTRACTION MANIFOLD – A manual vacuum manifold with large volume sampler for cartridge extractions, or an automatic/robotic sample preparation system designed for use with SPE cartridges, may be used if all QC requirements discussed in Section 9 are met. Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system. Care must be taken with automated SPE systems to ensure the PTFE commonly used in these systems does not contribute to unacceptable analyte concentrations in the MB (Sect. 9.2.1).

7.9.3 SAMPLE DELIVERY SYSTEM – Use of a polypropylene transfer tube system, which transfers the sample directly from the sample container to the SPE cartridge, is recommended, but not mandatory. Standard extraction manifolds come equipped with PTFE transfer tube systems. These can be replaced with 1/8” O.D. x 1/16” I.D. polypropylene or polyethylene tubing cut to an appropriate length to ensure no sample contamination from the sample transfer lines. Other types of non-PTFE tubing may be used provided it meets the MB (Sect. 9.2.1)

and LCS (Sect. 9.3) QC requirements. The PTFE transfer tubes may be used, but an MB must be run on each PFTE transfer tube and the QC requirements in Section 13.2.2 must be met. In the case of automated SPE, the removal of PTFE lines may not be feasible; therefore, MBs will need to be rotated among the ports and must meet the QC requirements of Sections 13.2.2 and 9.2.1.

7.10 EXTRACT CONCENTRATION SYSTEM – Extracts are concentrated by evaporation with nitrogen using a water bath set no higher than 65 °C.

7.11 LABORATORY OR ASPIRATOR VACUUM SYSTEM – Sufficient capacity to maintain a vacuum of approximately 10 to 15 inches of mercury for extraction cartridges.

7.12 LIQUID CHROMATOGRAPHY (LC)/TANDEM MASS SPECTROMETER (MS/MS) WITH DATA SYSTEM

7.12.1 LC SYSTEM – Instrument capable of reproducibly injecting up to 10-µL aliquots, and performing binary linear gradients at a constant flow rate near the flow rate used for development of this method (0.3 mL/min). The LC must be capable of pumping the water/methanol mobile phase without the use of a degasser which pulls vacuum on the mobile phase bottle (other types of degassers are acceptable). Degassers which pull vacuum on the mobile phase bottle will volatilize the ammonium acetate mobile phase causing the analyte peaks to shift to earlier retention times over the course of the analysis batch. The usage of a column heater is optional.

NOTE: During the course of method development, it was discovered that while idle for more than one day, PFASs built up in the PTFE solvent transfer lines. To prevent long delays in purging high levels of PFASs from the LC solvent lines, they were replaced with PEEK tubing and the PTFE solvent frits were replaced with stainless steel frits. It is not possible to remove all PFAS background contamination, but these measures help to minimize their background levels.

7.12.2 LC/TANDEM MASS SPECTROMETER – The LC/MS/MS must be capable of negative ion electrospray ionization (ESI) near the suggested LC flow rate of 0.3 mL/min. The system must be capable of performing MS/MS to produce unique product ions for the method analytes within specified retention time segments. A minimum of 10 scans across the chromatographic peak is required to ensure adequate precision.

7.12.3 DATA SYSTEM – An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored LC/MS/MS data by recognizing an LC peak within any given retention time window. The software must allow integration of the ion abundance of any specific ion within specified time or scan number limits. The software must be able to calculate relative response factors, construct linear regressions or quadratic calibration curves, and calculate analyte concentrations.

7.12.4 ANALYTICAL COLUMN – An LC C_{18} column (2.1 x 150 mm) packed with 5 µm d_p C_{18} solid phase particles was used. Any column that provides adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9) may be used.

8. Reagents and Standards

8.1 GASES, REAGENTS, AND SOLVENTS – Reagent grade or better chemicals should be used.

8.1.1 REAGENT WATER – Purified water which does not contain any measurable quantities of any method analytes or interfering compounds greater than 1/3 the RL for each method analyte of interest. Prior to daily use, at least 3 L of reagent water should be flushed from the purification system to rinse out any build-up of analytes in the system's tubing.

8.1.2 METHANOL (CH_3OH, CAS#: 67-56-1) – High purity, demonstrated to be free of analytes and interferences.

8.1.3 AMMONIUM ACETATE ($NH_4C_2H_3O_2$, CAS#: 631-61-8) – High purity, demonstrated to be free of analytes and interferences.

8.1.4 2 mM AMMONIUM ACETATE/REAGENT WATER – To prepare 1 L, add .154 g ammonium acetate to 1 L of reagent water. This solution is prone to volatility losses and should be replaced at least every 48 hours.

8.1.5 TRIZMA PRESET CRYSTALS, pH 7.0 – Reagent grade. A premixed blend of Tris [Tris(hydroxymethyl)aminomethane] and Tris HCL [Tris(hydroxymethyl)aminomethane hydrochloride]. Alternatively, a mix of the two components with a weight ratio of 15.5/1 Tris HCL/Tris may be used. These blends are targeted to produce a pH near 7.0 at 25 °C in reagent water. Trizma functions as a buffer, and removes free chlorine in chlorinated finished waters (Sect. 6.2.1).

8.1.6 NITROGEN – Used for the following purposes: Nitrogen aids in aerosol generation of the ESI liquid spray and is used as collision gas in some MS/MS instruments. The nitrogen used should meet or exceed instrument manufacturer's specifications. In addition, Nitrogen is used to concentrate sample extracts (Ultra High Purity or equivalent).

8.1.7 ARGON – Used as collision gas in MS/MS instruments. Argon should meet or exceed instrument manufacturer's specifications. Nitrogen gas may be used as the collision gas provided sufficient sensitivity (product ion formation) is achieved.

8.2 STANDARD SOLUTIONS – When a compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. PFAS analyte, IS and SUR standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in polypropylene containers. Standards for sample fortification generally should be prepared in the smallest volume that can be accurately measured to minimize the addition of excess organic solvent to aqueous samples.

NOTE: Stock standards (Sect. 8.2.1, 8.2.3 and 8.2.5) are stored at ≤4 °C. Primary dilution standards (Sect. 8.2.2 and 8.2.4) are stored at room temperature to prevent adsorption of the method analytes onto the container surfaces that may occur when refrigerated. Storing the standards at room temperature will also minimize daily imprecision due to the potential of inadequate room temperature stabilization.

8.2.1 IS STOCK STANDARD SOLUTIONS - IS stock standard solutions are stable for at least 6 months when stored at 4 °C. The stock solution is purchased at a concentration range of 1-4 ng/µl.

8.2.2 INTERNAL STANDARD PRIMARY DILUTION (IS PDS) STANDARD (0.5-2 ng/µL) – Prepare the IS PDS at a concentration of 0.5-2 ng/µL. The IS PDS is prepared in 96:4% (vol/vol) methanol:water. The IS PDS is stable for at least two months when stored in polypropylene centrifuge tubes at room temperature.

Table 3

Internal Standard	Conc. of IS Stock (ng/uL)	Vol. of IS Stock (mL)	Final Vol. of IS PDS (mL)	Final Conc. of IS PDS (ng/µL)
^{13}C-PFOA	1	1.0	2.0	0.5
^{13}C-PFOS	3	1.0	2.0	1.5
d_3-NMeFOSAA	4	1.0	2.0	2.0

8.2.3 SUR STOCK STANDARD SOLUTIONS – SUR stock standard solutions are stable for at least 6 months when stored at 4 °C.

8.2.4 SURROGATE PRIMARY DILUTION STANDARD (SUR PDS) (0.5-2 ng/µL) – Prepare the SUR PDS at a concentration of 0.5-2 ng/µL. The SUR PDS is prepared in 96:4% (vol/vol) methanol:water. This solution is used to fortify all QC and Field Samples. The PDS is stable for one year when stored in polypropylene centrifuge tubes at room temperature.

Table 4

Surrogate	Conc. of SUR Stock (ng/µL)	Vol. of SUR Stock (mL)	Final Vol. of SUR PDS (,L)	Final Conc. of SUR PDS (ng/µL)
^{13}C-PFHxA	1.0	1.0	2.0	0.5
^{13}C-PFDA	1.0	1.0	2.0	0.5
d_5-NEtFOSAA	4.0	1.0	2.0	2.0
Tetrafluoro-2-heptafluoropropoxy-13C3-propanoic acid[1]	50	1.0	2.0	0.5

[1] EPA 537.1 Surrogate only

8.2.5 ANALYTE STOCK STANDARD SOLUTION – Analyte stock standards are stable for at least 6 months when stored at -15 °C. When using these stock standards to prepare a PDS, care must be taken to ensure that these standards are at room temperature and adequately vortexed.

Table 5

Analyte	Analyte Stock Solvent	Concentration (ug/mL)
PFHxA	100% methanol	1.0
PFHpA	100% methanol	1.0
PFOA	100% methanol	1.0
PFNA	100% methanol	1.0
PFDA	100% methanol	1.0
PFUnA	100% methanol	1.0
PFDoA	100% methanol	1.0
PFTrDA	100% methanol	1.0
PFTA	100% methanol	1.0
PFBS	100% methanol	1.0

Table 5 (cont.)

Analyte	Analyte Stock Solvent	Concentration (ug/mL)
PFHxS	100% methanol	1.0
PFOS	100% methanol	1.0
NEtFOSAA	100% methanol	1.0
NMeFOSAA	100% methanol	1.0
HFPO-DA	100% methanol	50.0
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	100% methanol	50.0
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	100% methanol	50.0
4,8-dioxa-3H-perfluorononanoic acid	100% methanol	50.0

8.2.6 LOW, MEDIUM AND HIGH LEVEL LCS – The LCS's will be prepared at the following concentrations and rotated per batch; 2 ng/L, 40 ng/L, 500 ng/l. The analyte PDS contains all the method analytes of interest at various concentrations in methanol containing 4% water. The analyte PDS has been shown to be stable for 6 months when stored at room temperature.

8.2.7 CALIBRATION STANDARDS (CAL) –

Current Concentrations (ng/mL): 0.5, 1.0, 5.0, 10.0, 50.0, 125 and 150 (optional)

Prepare the CAL standards over the concentration range of interest from dilutions of the analyte PDS in methanol containing 4% reagent water. The IS and SUR are added to the CAL standards at a constant concentration (10-40 ng/L). The lowest concentration CAL standard must be at or below the RL (2 ng/L), which may depend on system sensitivity. The CAL standards may also be used as CCVs (Sect. 9.9). The CAL standards are stable for at least two weeks when stored at room temperature. Longer storage times are acceptable provided appropriate QC measures are documented demonstrating the CAL standard stability.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 REPORTING LIMIT (RL) CONFIRMATION

9.1.1 Fortify, extract, and analyze seven replicate LCSs at 2 ng/l. These LCSs must contain all method preservatives described in Section 6.2.1. Calculate the mean measured concentration (*Mean*) and standard deviation for these replicates. Determine the Half Range for the prediction interval of results (HR_{PIR}) using the equation below

$$HR_{PIR} = 3.963s$$

Where:

s = the standard deviation
3.963 = a constant value for seven replicates.

9.1.2 Confirm that the upper and lower limits for the Prediction Interval of Result (*PIR* = *Mean* ± HR_{PIR}) meet the upper and lower recovery limits as shown below

The Upper PIR Limit must be ≤150% recovery.

$$\frac{Mean + HR_{PIR}}{Fortified\ Concentration} \times 100\% \leq 150\%$$

The Lower PIR Limit must be ≥ 50% recovery.

$$\frac{Mean - HR_{PIR}}{Fortified\ Concentration} \times 100\% \geq 50\%$$

9.1.3 The RL is validated if both the Upper and Lower PIR Limits meet the criteria described above. If these criteria are not met, the RL has been set too low and must be determined again at a higher concentration.

9.2 Blank(s)

9.2.1 **METHOD BLANK (MB) -** A Method Blank (MB) is required with each extraction batch to confirm that potential background contaminants are not interfering with the identification or quantitation of method analytes. If more than 20 Field Samples are included in a batch, analyze an MB for every 20 samples. If the MB produces a peak within the retention time window of any analyte that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding. Background from method analytes or other contaminants that interfere with the measurement of method analytes must be below 1/3 of the RL. Blank contamination is estimated by extrapolation, if the concentration is below the lowest CAL standard. This extrapolation procedure is not allowed for sample results as it may not meet data quality objectives. If the method analytes are detected in the MB at concentrations equal to or greater than this level, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch. Because background contamination is a significant problem for several method analytes, it is highly recommended that the analyst maintain a historical record of MB data.

9.2.2 **FIELD REAGENT BLANK (FRB)** - The purpose of the FRB is to ensure that PFASs measured in the Field Samples were not inadvertently introduced into the sample during sample collection/handling. Analysis of the FRB is required only if a Field Sample contains a method analyte or analytes at or above the RL. The FRB is processed, extracted and analyzed in exactly the same manner as a Field Sample. If the method analyte(s) found in the Field Sample is present in the FRB at a concentration greater than 1/3 the RL, then all samples collected with that FRB are invalid and must be recollected and reanalyzed.

9.3 Laboratory Control Sample (LCS)

9.3.1 An LCS is required with each extraction batch. The fortified concentration of the LCS must be rotated between low, medium, and high concentrations from batch to batch.

9.3.2 The low concentration LCS must be as near as practical to, but no more than two times, the RL. Similarly, the high concentration LCS should be near the high end of the calibration range established during the initial calibration (Sect. 10.6).

9.3.3 Results of the low-level LCS analyses must be 50-150% of the true value. Results of the medium and high-level LCS analyses must be 70-130% of the true value. If the LCS results do not meet these criteria for method analytes, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch.

9.3.4 It is the responsibility of the extraction chemist to view the previous extraction batch to determine the next spiking concentration. (Low → Medium → High)

9.4 Internal Standards (IS)

The analyst must monitor the peak areas of the IS(s) in all injections during each analysis day. The IS responses (peak areas) in any chromatographic run must be within 70-140% of the response in the most recent CCV and must not deviate by more than 50% from the average area measured during initial analyte calibration. If the IS areas in a chromatographic run do not meet these criteria, inject a second aliquot of that extract aliquoted into a new capped autosampler vial. Random evaporation losses have been observed with the polypropylene caps causing high IS(s) areas.

9.4.1 If the reinjected aliquot produces an acceptable IS response, report results for that aliquot.

9.4.2 If the reinjected extract fails again, the analyst should check the calibration by reanalyzing the most recently acceptable CAL standard. If the CAL standard fails the criteria of Section 9.9, recalibration is in order per Section 10.6. If the CAL standard is acceptable, extraction of the sample may need to be repeated provided the sample is still within the holding time. Otherwise, report results obtained from the reinjected extract, but annotate as suspect. Alternatively, collect a new sample and re-analyze.

9.5 Surrogate Recovery

The SUR standard is fortified into all samples, CCVs, MBs, LCSs, MSs, MSDs, FD, and FRB prior to extraction. It is also added to the CAL standards. The SUR is a means of assessing method performance from extraction to final chromatographic measurement. Calculate the recovery (%R) for the SUR using the following equation

$$\%R = (A / B) \times 100$$

Where:

A = calculated SUR concentration for the QC or Field Sample
B = fortified concentration of the SUR.

9.5.1.1 SUR recovery must be in the range of 70-130%. When SUR recovery from a sample, blank, or CCV is less than 70% or greater than 130%, check 1) calculations to locate possible errors, 2) standard solutions for degradation, 3) contamination, and 4) instrument performance. Correct the problem and reanalyze the extract.

9.5.1.2 If the extract reanalysis meets the SUR recovery criterion, report only data for the reanalyzed extract.

9.5.1.3 If the extract reanalysis fails the 70-130% recovery criterion, the analyst should check the calibration by injecting the last CAL standard that passed. If the CAL standard fails the criteria of Section 10.7, recalibration is in order per Section 10.6. If the CAL standard is acceptable, extraction of the sample should be repeated provided the sample is still within the holding time. If the re-extracted sample also fails the recovery criterion, report all data for that sample as suspect/SUR recovery to inform the data user that the results are suspect due to SUR recovery. Alternatively, collect a new sample and re-analyze.

9.6 Matrix Spike (MS)

9.6.1 Analysis of an MS is required in each extraction batch and is used to determine that the sample matrix does not adversely affect method accuracy. Assessment of method precision is accomplished by analysis of a Field Duplicate (FD) (Sect. 9.7); however, infrequent occurrence of method analytes would hinder this assessment. If the occurrence of method analytes in the samples is infrequent, or if historical trends are unavailable, a second MS, or MSD, must be prepared, extracted, and analyzed from a duplicate of the Field Sample. Extraction batches that contain MSDs will not require the extraction of a field sample duplicate. If a variety of different sample matrices are analyzed regularly, for example, groundwater and surface water sources, method performance should be established for each. Over time, MS data should be documented by the laboratory for all routine sample sources.

9.6.2 Within each extraction batch, a minimum of one Field Sample is fortified as an MS for every 20 Field Samples analyzed. The MS is prepared by spiking a sample with an appropriate amount of the Analyte Stock Standard (Sect. 8.2.5). Use historical data and rotate through the low, mid and high concentrations when selecting a fortifying concentration. Calculate the percent recovery (%*R*) for each analyte using the equation

$$\%R = \frac{(A - B)}{C} \times 100$$

Where:

A = measured concentration in the fortified sample
B = measured concentration in the unfortified sample
C = fortification concentration.

9.6.3 Analyte recoveries may exhibit matrix bias. For samples fortified at or above their native concentration, recoveries should range between 70-130%, except for low-level fortification near or at the RL (within a factor of 2-times the RL concentration) where 50-150% recoveries are acceptable. If the accuracy of any analyte falls outside the designated range, and the laboratory performance for

that analyte is shown to be in control in the CCVs, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.7 Laboratory Duplicate

9.7.1 FIELD DUPLICATE OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (FD or MSD) – Within each extraction batch (not to exceed 20 Field Samples), a minimum of one FD or MSD must be analyzed. Duplicates check the precision associated with sample collection, preservation, storage, and laboratory procedures. If method analytes are not routinely observed in Field Samples, an MSD should be analyzed rather than an FD.

9.7.2 Calculate the relative percent difference (*RPD*) for duplicate measurements (*FD1* and *FD2*) using the equation

$$RPD = \frac{|FD1 - FD2|}{(FD1 + FD2) / 2} \times 100$$

9.7.3 RPDs for FDs should be ≤30%. Greater variability may be observed when FDs have analyte concentrations that are within a factor of 2 of the RL. At these concentrations, FDs should have RPDs that are ≤50%. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCV, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.7.4 If an MSD is analyzed instead of a FD, calculate the relative percent difference (RPD) for duplicate MSs (MS and MSD) using the equation

$$RPD = \frac{|MS - MSD|}{(MS + MSD) / 2} \times 100$$

9.7.5 RPDs for duplicate MSs should be ≤30% for samples fortified at or above their native concentration. Greater variability may be observed when MSs are fortified at analyte concentrations that are within a factor of 2 of the RL. MSs fortified at these concentrations should have RPDs that are ≤50% for samples fortified at or above their native concentration. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCV, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.8 Initial Calibration Verification (ICV)

9.8.1 As part of the IDC (Sect. 13.2), each time a new Analyte Stock Standard solution (Sect. 8.2.5) is used, and at least quarterly, analyze a QCS sample from a source different from the source of the CAL standards. If a second vendor is not available, then a different lot of the standard should be used. The QCS should be prepared and analyzed just like a CCV. Acceptance criteria for the QCS are identical to the CCVs; the calculated amount for each analyte must be ± 30% of the expected value. If measured analyte concentrations are not of acceptable

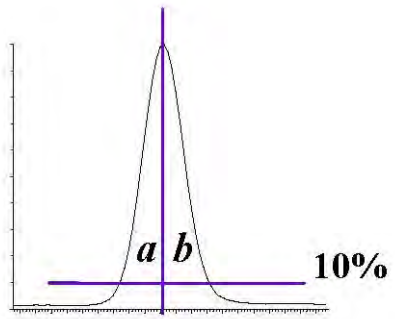
accuracy, check the entire analytical procedure to locate and correct the problem.

9.9 Continuing Calibration Verification (CCV)

9.9.1 CCV Standards are analyzed at the beginning of each analysis batch, after every 10 Field Samples, and at the end of the analysis batch. See Section 10.7 for concentration requirements and acceptance criteria.

9.10 Method-specific Quality Control Samples

9.10.1 PEAK ASYMMETRY FACTOR – A peak asymmetry factor must be calculated using the equation below during the IDL and every time a calibration curve is generated. The peak asymmetry factor for the first two eluting peaks in a midlevel CAL standard (if only two analytes are being analyzed, both must be evaluated) must fall in the range of 0.8 to 1.5. Modifying the standard or extract composition to more aqueous content to prevent poor shape is not permitted. See guidance in Section 10.6.4.1 if the calculated peak asymmetry factors do not meet the criteria.



$$A_s = b / a$$

Where:

A_s = peak asymmetry factor
b = width of the back half of the peak measured (at 10% peak height) from the trailing edge of the peak to a line dropped perpendicularly from the peak apex
a = the width of the front half of the peak measured (at 10% peak height) from the leading edge of the peak to a line dropped perpendicularly from the apex.

9.11 Method Sequence

ICV

CCV-LOW

MB

LCS

LCSD

MS

Duplicate or MSD

Field Samples (1-10)

CCV-MID

Field Samples (11-20)

CCV-HIGH

10. Procedure

10.1 Equipment Set-up

10.1.1 This procedure may be performed manually or in an automated mode using a robotic or automatic sample preparation device. If an automated system is used to prepare samples, follow the manufacturer's operating instructions, but all extraction and elution steps must be the same as in the manual procedure. Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system. If an automated system is used, the MBs should be rotated among the ports to ensure that all the valves and tubing meet the MB requirements (Sect. 9.2).

10.1.2 Some of the PFASs adsorb to surfaces, including polypropylene. Therefore, the aqueous sample bottles must be rinsed with the elution solvent (Sect 10.3.4) whether extractions are performed manually or by automation. The bottle rinse is passed through the cartridge to elute the method analytes and is then collected (Sect. 10.3.4).

10.1.3 **NOTE:** The SPE cartridges and sample bottles described in this section are designed as single use items and should be discarded after use. They may not be refurbished for reuse in subsequent analyses.

10.2 Sample Preparation

10.2.1 Samples are preserved, collected and stored as presented in Section 6. All Field and QC Samples, including the MB, LCS and FRB, must contain the dechlorinating agent listed in Section 6.2.1. Determine sample volume. An indirect measurement may be done in one of two ways: by marking the level of the sample on the bottle or by weighing the sample and bottle to the nearest 10 g. After extraction, proceed to Section 10.5 for final volume determination. Some of the PFASs adsorb to surfaces, thus the sample volume may **NOT** be transferred to a graduated cylinder for volume measurement. The MB, LCS and FRB may be prepared by measuring 250 mL of reagent water with a polypropylene graduated cylinder or filling a 250-mL sample bottle to near the top.

The entire sample that is received must be sent through the SPE cartridge. In addition, the bottle must be solvent rinsed and this rinse must be sent through the SPE cartridge as well. The method blank (MB) and laboratory control sample (LCS) must be extracted in exactly the same manner (i.e., must include the bottle solvent rinse). It should be noted that a water rinse alone is not sufficient. This does not apply to samples with high concentrations of PFAS that are prepared using serial dilution and not SPE.

10.2.2 Add 20 µL of the SUR PDS (Sect. 8.2.4) to each sample, cap and invert to mix for a final concentration of 10 ng/L for ^{13}C-PFHxA and ^{13}C-PFDA and 40 ng/L for d_5-NEtFOSAA.

10.2.3 In addition to the SUR(s) and dechlorination agent, if the sample is an LCS, MS, or MSD, add the necessary amount of analyte PDS (Sect. 8.2.5). Cap and invert each sample to mix.

10.3 Cartridge SPE Procedure

10.3.1 CARTRIDGE CLEAN-UP AND CONDITIONING – DO NOT allow cartridge packing material to go dry during any of the conditioning steps. Rinse each cartridge with 15 mL of methanol. Next, rinse each cartridge with 18 mL of reagent water, without allowing the water to drop below the top edge of the packing. If the cartridge goes dry during the conditioning phase, the conditioning must be started over. Add 4-5 mL of reagent water to each cartridge, attach the sample transfer tubes (Sect. 7.2.3), turn on the vacuum, and begin adding sample to the cartridge.

10.3.2 SAMPLE EXTRACTON – Adjust the vacuum so that the approximate flow rate is 10-15 mL/min. Do not allow the cartridge to go dry before all the sample has passed through.

10.3.3 SAMPLE BOTTLE AND CARTRIDGE RINSE – After the entire sample has passed through the cartridge, rinse the sample bottles with two 7.5-mL aliquots of reagent water and draw each aliquot through the sample transfer tubes and the cartridges. Draw air or nitrogen through the cartridge for 5 min at high vacuum (10-15 in. Hg).

NOTE: If empty plastic reservoirs are used in place of the sample transfer tubes to pass the samples through the cartridges, these reservoirs must be treated like the transfer tubes. After the entire sample has passed through the cartridge, the reservoirs must be rinsed to waste with reagent water.

10.3.4 SAMPLE BOTTLE AND CARTRIDGE ELUTION – Turn off and release the vacuum. Lift the extraction manifold top and insert a rack with collection tubes into the extraction tank to collect the extracts as they are eluted from the cartridges. Rinse the sample bottles with 4 mL of methanol and elute the analytes from the cartridges by pulling the 4 mL of methanol through the sample transfer tubes and the cartridges. Use a low vacuum such that the solvent exits the cartridge in a dropwise fashion. Repeat sample bottle rinse and cartridge elution with a second 4-mL aliquot of methanol.

NOTE: If empty plastic reservoirs are used in place of the sample transfer tubes to pass the samples through the cartridges, these reservoirs must be treated like the transfer tubes. After the reservoirs have been rinsed in Section 10.3.3, the elution solvent used to rinse the sample bottles must be swirled down the sides of the reservoirs while eluting the cartridge to ensure that any method analytes on the surface of the reservoirs are transferred to the extract.

10.4 Extract Concentration

10.4.1 Concentrate the extract to dryness under a gentle stream of nitrogen in a heated water bath (60-65 °C) to remove all the water/methanol mix. Add the appropriate amount of 96:4% (vol/vol) methanol:water solution and the IS PDS (Sect. 8.2.2) to the collection vial to bring the volume to 1 mL and vortex. Transfer a small aliquot with a plastic pipet (Sect. 7.6) to a polypropylene autosampler vial.

NOTE: It is recommend that the entire 1-mL aliquot not be transferred to the autosampler vial because the polypropylene autosampler caps do not reseal after injection. Therefore, do not store the extracts in the autosampler vials as evaporation losses can occur occasionally in these

autosampler vials. Extracts can be stored in 15-mL centrifuge tubes (Sect. 7.3).

10.5 Sample Volume Determination

10.5.1 If the level of the sample was marked on the sample bottle, use a graduated cylinder to measure the volume of water required to fill the original sample bottle to the mark made prior to extraction. Determine to the nearest 10 mL. If using weight to determine volume, weigh the empty bottle to the nearest 10 g and determine the sample weight by subtraction of the empty bottle weight from the original sample weight (Sect. 10.2.1). Assume a sample density of 1.0 g/mL. In either case, the sample volume will be used in the final calculations of the analyte concentration (Sect. 11.2).

10.6 Initial Calibration - Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. After the initial calibration is successful, a CCV is required at the beginning and end of each period in which analyses are performed, and after every tenth Field Sample.

10.6.1 ESI-MS/MS TUNE

10.6.1.1 Calibrate the mass scale of the MS with the calibration compounds and procedures prescribed by the manufacturer.

10.6.1.2 Optimize the [M-H]- for each method analyte by infusing approximately 0.5-1.0 µg/mL of each analyte (prepared in the initial mobile phase conditions) directly into the MS at the chosen LC mobile phase flow rate (approximately 0.3 mL/min). This tune can be done on a mix of the method analytes. The MS parameters (voltages, temperatures, gas flows, etc.) are varied until optimal analyte responses are determined. The method analytes may have different optima requiring some compromise between the optima.

10.6.1.3 Optimize the product ion for each analyte by infusing approximately 0.5-1.0 µg/mL of each analyte (prepared in the initial mobile phase conditions) directly into the MS at the chosen LC mobile phase flow rate (approximately 0.4 mL/min). This tune can be done on a mix of the method analytes. The MS/MS parameters (collision gas pressure, collision energy, etc.) are varied until optimal analyte responses are determined. Typically, the carboxylic acids have very similar MS/MS conditions and the sulfonic acids have similar MS/MS conditions.

10.6.2 Establish LC operating parameters that optimize resolution and peak shape. Modifying the standard or extract composition to more aqueous content to prevent poor shape is not permitted.

Cautions: LC system components, as well as the mobile phase constituents, contain many of the method analytes in this method. Thus, these PFASs will build up on the head of the LC column during mobile phase equilibration. To minimize the background PFAS peaks and to keep background levels constant, the time the LC column sits at initial conditions must be kept constant and as short as possible (while ensuring reproducible retention times). In addition, prior to daily use, flush the column with 100% methanol for at least 20 min before initiating a sequence. It may be necessary on some systems to flush other LC components such as wash

syringes, sample needles or any other system components before daily use.

Mobile phase modifiers other than 20 mM ammonium acetate may be used at the discretion of the analyst, provided that the retention time stability criteria in Sect. 10.9.2 can be met over a period of two weeks. During method development, retention times shifted to shorter and shorter times as days progressed when mobile phases with less than 20 mM ammonium acetate were used.

10.6.3 Inject a mid-level CAL standard under LC/MS conditions to obtain the retention times of each method analyte. If analyzing for PFTA, ensure that the LC conditions are adequate to prevent co-elution of PFTA and the mobile phase interferants. These interferants have the same precursor and products ions as PFTA, and under faster LC conditions may co-elute with PFTA. Divide the chromatogram into retention time windows each of which contains one or more chromatographic peaks. During MS/MS analysis, fragment a small number of selected precursor ions ([M-H]-) for the analytes in each window and choose the most abundant product ion. For maximum sensitivity, small mass windows of ±0.5 daltons around the product ion mass were used for quantitation. If sufficient sensitivity exists to meet the RL, wider mass ranges may be used to obtain more confirmation ions.

10.6.3.1 As recommended by the EPA Advisory on September 2016, both linear and branched isomers should be included in the quantitation. NOTE: As the NOTE in Section 10.6.4.1 indicates, PFOS has linear and branched isomers. There have been reports that not all the products ions in the linear PFOS are produced in all the branched PFOS isomers. (This phenomenon probably exists for PFHxS and PFBS also, although it has not been studied to date.) Thus, in an attempt to reduce PFOS bias, it is required that the *m/z* 499 → *m/z* 80 transition be used as the quantitation transition. Some MS/MS instruments, such as conventional ion traps, may not be able to scan a product ion with such a wide mass difference from the precursor ion; therefore, they may not be used for this method if PFOS, PFBS, or PFHxS analysis is to be conducted. Literature reports indicate for the most abundant PFOS isomer, which is the linear isomer, that all the products ions obtained on an ion trap have less than 10% relative abundance. In addition, there is not a single ion trap MS/MS transition that encompasses the linear isomer and the majority of the branch isomers; thus, the bias would be unacceptably high.

10.6.4 Inject a mid-level CAL standard under optimized LC/MS/MS conditions to ensure that each method analyte is observed in its MS/MS window and that there are at least 10 scans across the peak for optimum precision.

10.6.4.1 If broad, split or fronting peaks are observed for the first two eluting chromatographic peaks (if only two analytes are being analyzed, both must be evaluated), change the initial mobile phase conditions to higher aqueous content until the peak asymmetry ratio for each peak is 0.8 – 1.5. The peak asymmetry factor is calculated as described in Section 9.10.1 on a mid-level CAL standard. The peak asymmetry factor must meet the above criteria for the first two eluting peaks during the IDL and every time a new calibration curve is generated. Modifying the standard

or extract composition to more aqueous content to prevent poor shape is not permitted.

NOTE: PFHxS, PFOS, NMeFOSAA, and NEtFOSAA have multiple chromatographic peaks using the LC conditions in Table 5 due to chromatographic resolution of the linear and branched isomers of these compounds. According to the EPA Advisory, September 2016, the branched isomers are identified by analyzing a qualitative/semi-qualitative mixed PFOA standard and the quantitation of PFOA is accomplished by integration the total response which includes peaks identified as linear and branched isomers. Most PFASs are produced by two different processes. One process gives rise to linear PFASs only while the other process produces both linear and branched isomers. Thus, both branched and linear PFASs can potentially be found in the environment. For the aforementioned compounds that give rise to more than one peak, all the chromatographic peaks observed in the standard must be integrated and the areas totaled. Chromatographic peaks in a sample must be integrated in the same way as the CAL standard.

10.6.5 Prepare a set of CAL standards as described in Section 8.2.7. The lowest concentration CAL standard must be at or below the RL (2 ng/L), which may depend on system sensitivity. It is recommended that at least four of the CAL standards are at a concentration greater than or equal to the RL.

10.6.6 The LC/MS/MS system is calibrated using the IS technique. Use the LC/MS/MS data system software to generate a linear regression or quadratic calibration curve for each of the analytes. This curve **must always** be forced through zero and may be concentration weighted, if necessary. Forcing zero allows for a better estimate of the background levels of method analytes.

10.6.6.1 The isotopically labeled IS(s) in this method may undergo suppression in the ESI source if the concentration of the co-eluting unlabeled method analyte(s) is too high. The analyte concentration at which suppression may occur can vary depending on the instrument, LC conditions, ESI conditions, IS concentration, etc. To evaluate whether suppression is occurring during calibration, calculate the relative percent difference (*RPD*) between the high (H) and low (L) areas for each IS using the equation

$$RPD = \frac{(H - L)}{(H + L) / 2} \times 100$$

10.6.6.2 The RPD calculated above must be <20% for each IS during calibration. If the calculated RPD is >20% for any IS, the analyst must recalibrate at lower analyte concentrations until the IS RPDs are <20%.

10.6.7 CALIBRATION ACCEPTANCE CRITERIA – When quantitated using the initial calibration curve, each calibration point, except the lowest point, for each analyte should calculate to be within 70-130% of its true value. The lowest CAL point should calculate to be within 50-150% of its true value. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. It is recommended that corrective action is taken to reanalyze the CAL standards, restrict the range of calibration, or select an alternate method of calibration (forcing the curve through zero is still required).

10.6.7.1 CAUTION: When acquiring MS/MS data, LC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times. If this is not done, the correct ions will not be monitored at the appropriate times. As a precautionary measure, the chromatographic peaks in each window must not elute too close to the edge of the segment time window.

10.7 CONTINUING CALIBRATION CHECK (CCV) – Minimum daily calibration verification is as follows. Verify the initial calibration at the beginning and end of each group of analyses, and after every tenth sample during analyses. In this context, a "sample" is considered to be a Field Sample. MBs, CCVs, LCSs, MSs, FDs FRBs and MSDs are not counted as samples. The beginning CCV of each analysis batch must be at or below the RL in order to verify instrument sensitivity prior to any analyses. If standards have been prepared such that all low CAL points are not in the same CAL solution, it may be necessary to analyze two CAL standards to meet this requirement. Alternatively, the analyte concentrations in the analyte PDS may be customized to meet this criterion. Subsequent CCVs should alternate between a medium and high concentration CAL standard.

10.7.1 Inject an aliquot of the appropriate concentration CAL standard and analyze with the same conditions used during the initial calibration.

10.7.2 Determine that the absolute areas of the quantitation ions of the IS(s) are within 70-140% of the areas measured in the most recent continuing calibration check, and within 50-150% from the average areas measured during initial calibration. If any of the IS areas has changed by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may include cleaning of the MS ion source, or other maintenance as indicated in Section 10.7.4. Major instrument maintenance requires recalibration (Sect 10.6) and verification of sensitivity by analyzing a CCV at or below the RL (Sect 10.7). Control charts are useful aids in documenting system sensitivity changes.

10.7.3 Calculate the concentration of each analyte and SUR in the CCV. The calculated amount for each analyte and SUR for medium and high level CCVs must be within ± 30% of the true value. The calculated amount for the lowest calibration point for each analyte must be within ± 50% and the SUR must be within ± 30% of the true value. If these conditions do not exist, then all data for the problem analyte must be considered invalid, and remedial action should be taken (Sect. 10.7.4) which may require recalibration. Any Field or QC Samples that have been analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored, with the following exception. **If the CCV fails because the calculated concentration is greater than 130% (150% for the low-level CCV) for a particular method analyte, and Field Sample extracts show no detection for that method analyte, non-detects may be reported without re-analysis.**

10.7.4 REMEDIAL ACTION – Failure to meet CCV QC performance criteria may require remedial action. Major maintenance, such as cleaning the electrospray probe, atmospheric pressure ionization source, cleaning the mass analyzer, replacing the LC column, etc., requires recalibration (Sect 10.6) and verification of sensitivity by analyzing a CCV at or below the RL (Sect 10.7).

10.8 EXTRACT ANALYSIS

10.8.1 Establish operating conditions equivalent to those summarized in Tables 5-8 of Section 16. Instrument conditions and columns should be optimized prior to the initiation of the IDC.

10.8.2 Establish an appropriate retention time window for each analyte. This should be based on measurements of actual retention time variation for each method analyte in CAL standard solutions analyzed on the LC over the course of time. A value of plus or minus three times the standard deviation of the retention time obtained for each method analyte while establishing the initial calibration and completing the IDC can be used to calculate a suggested window size. However, the experience of the analyst should weigh heavily on the determination of the appropriate retention window size.

10.8.3 Calibrate the system by either the analysis of a calibration curve (Sect. 10.6) or by confirming the initial calibration is still valid by analyzing a CCV as described in Section 10.7. If establishing an initial calibration, complete the IDC as described in Section 13.2.

10.8.4 Begin analyzing Field Samples, including QC samples, at their appropriate frequency by injecting the same size aliquots, under the same conditions used to analyze the CAL standards.

10.8.5 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to identify peaks of interest in predetermined retention time windows. Use the data system software to examine the ion abundances of the peaks in the chromatogram. Identify an analyte by comparison of its retention time with that of the corresponding method analyte peak in a reference standard.

10.8.6 Comparison of the MS/MS mass spectra is not particularly useful given the limited ±0.5 dalton mass range around a single product ion for each method analyte.

10.8.7 The analyst must not extrapolate beyond the established calibration range. If an analyte peak area exceeds the range of the initial calibration curve, the extract may be diluted with 96%:4% vol/vol) methanol:water solution and the appropriate amount of IS added to match the original concentration. Re-inject the diluted extract. Incorporate the dilution factor into the final concentration calculations. Acceptable SUR performance (Sect. 9.5.1.1) should be determined from the undiluted sample extract. The resulting data should be documented as a dilution, with an increased RL.

11. Data Evaluation, Calculations and Reporting

11.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations using MS/MS. In validating this method, concentrations were calculated by measuring the product ions listed in Table 8. Other ions may be selected at the discretion of the analyst.

11.2 Calculate analyte and SUR concentrations using the multipoint calibration established in Section 10.6. Do not use daily calibration verification data to quantitate analytes in samples. Adjust final analyte concentrations to reflect the actual sample volume determined in Section 10.5.

11.3 Prior to reporting the data, the chromatogram should be reviewed for any incorrect peak identification or poor integration.

11.4 PFHxS, PFOS, NMeFOSAA, and NEtFOSAA have multiple chromatographic peaks using the LC conditions in Table 5 due to the linear and branch isomers of these compounds (Sect. 10.6.4.1). The areas of all the linear and branched isomer peaks observed in the CAL standards for each of these analytes must be summed and the concentrations reported as a total for each of these analytes.

11.5 Calculations must utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

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

12.1 Section 9.0 outlines sample batch QC acceptance criteria. If non-compliant organic compound results are to be reported, the Organic Section Head and/or the Laboratory Director, and the Operations Manager must approve the reporting of these results. The laboratory Project Manager shall be notified, and may choose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The analyst, Data Reviewer, or Department Supervisor performing the secondary review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

12.2 All results for the organic compounds of interest are reportable without qualification if extraction and analytical holding times are met, preservation requirements (including cooler temperatures) are met, all QC criteria defined in the table below are met, and matrix interference is not suspected during extraction or analysis of the samples. If any of the below QC parameters are not met, all associated samples must be evaluated for re-extraction and/or re-analysis.

13. Method Performance

13.1 Detection Limit Study (DL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

13.1.1 The laboratory follows the procedure to determine the DL, LOD, and/or LOQ as outlined in Alpha SOP ID 1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

13.2.1 The IDC must be successfully performed prior to analyzing any Field Samples. Prior to conducting the IDC, the analyst must first generate an acceptable Initial Calibration following the procedure outlined in Section 10.6.

13.2.2 INITIAL DEMONSTRATION OF LOW SYSTEM BACKGROUND – Any time a new lot of SPE cartridges, solvents, centrifuge tubes, disposable pipets, and autosampler vials are used, it must be demonstrated that an MB is reasonably free of contamination and that the criteria in Section 9.2.1 are met. If an automated extraction system is used, an MB should be extracted on each port to ensure that all the valves and tubing are free from potential PFAS contamination.

13.2.3 INITIAL DEMONSTRATION OF PRECISION (IDP) – Prepare, extract, and analyze four to seven replicate LCSs fortified near the midrange of the initial calibration curve according to the procedure described in Section 10. Sample preservatives as described in Section 6.2.1 must be added to these samples. The relative standard deviation (RSD) of the results of the replicate analyses must be less than 20%.

13.2.4 INITIAL DEMONSTRATION OF ACCURACY (IDA) – Using the same set of replicate data generated for Section 13.2.3, calculate average recovery. The average recovery of the replicate values must be within ± 30% of the true value.

13.2.5 INITIAL DEMONSTRATION OF PEAK ASYMMETRY FACTOR – Peak asymmetry factors must be calculated using the equation in Section 9.10.1 for the first two eluting peaks (if only two analytes are being analyzed, both must be evaluated) in a mid-level CAL standard. The peak asymmetry factors must fall in the range of 0.8 to 1.5. See guidance in Section 10.6.4.1 if the calculated peak asymmetry factors do not meet the criteria.

13.2.6 Refer to Alpha SOP ID 1739 for further information regarding IDC/DOC Generation.

13.2.7 The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

14.1 Refer to Alpha's Chemical Hygiene Plan and Hazardous Waste Management and Disposal SOP for further pollution prevention and waste management information.

14.2 This method utilizes SPE to extract analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby minimizing the potential hazards to both the analyst and the environment as compared to the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.3 The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents and solvents are used. However, laboratory waste management practices must be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

15. Referenced Documents

15.1 Chemical Hygiene Plan – ID 2124

15.2 SOP ID 1732 Detection Limit (DL), Limit of Detection (LOD) & Limit of Quantitation (LOQ) SOP

15.3 SOP ID 1739 Demonstration of Capability (DOC) Generation SOP

15.4 SOP ID 1728 Hazardous Waste Management and Disposal SOP

16. Attachments

Table 6: LC Method Conditions

Time (min)	2 mM Ammonium Acetate (5:95 MeOH/H_2O)	2 mM Ammonium Acetate (100% Methanol)
Initial	100.0	0.0
1.0	100.0	0.0
2.2	85.0	15.0
11	20.0	80.0
11.4	0.0	100.0
12.4	100.0	0.0
14.0	100.0	0.0
Waters Aquity UPLC ® BEHC_{18} 2.1 x 50 mm packed with 1.7 µm BEH C_{18} stationary phase Flow rate of 0.4 mL/min 2-5 µL injection		

Table 7: ESI-MS Method Conditions

ESI Conditions	
Polarity	Negative ion
Capillary needle voltage	.5 kV
Cone Gas Flow	20 L/hr
Nitrogen desolvation gas	1100 L/hr
Desolvation gas temp.	500 ºC

Table 8: Method Analyte Source, Retention Times (RTs), and IS References

Analyte	Peak #	IS# Ref
PFBS	1	2
PFHxA	3	1
HFPO-DA	5	1
PFHpA	6	1
PFHxS	7	2
ADONA	8	1
PFOA	10	1
PFNA	11	1
PFOS	12	2
PFDA	14	1
9CL-PF3ONS	15	1
NMeFOSAA	17	3
PFUnA	18	3
NEtFOSAA	20	1
PFDoA	21	1
11CL-PFOUdS	22	1
PFTrDA	23	1
PFTA	24	1
^{13}C-PFHxA	2	1
^{13}C-HFPO-DA	4	1
^{13}C-PFDA	13	1
d_5-NEtFOSAA	19	3
^{13}C-PFOA-IS#1	9	-
^{13}C-PFOS-IS#2	10	-
d_3-NMeFOSAA-IS#3	16	-

Table 9: MS/MS Method Conditions

Segment[a]	Analyte	Precursor Ion [b] (m/z)	Product Ion [b,c] (m/z)
1	PFBS	299	80
2	PFHxA	313	269
4	HFPO-DA	285	169
5	PFHpA	363	319
6	PFHxS [e]	399	80
7	ADONA	377	251
9	PFOA	413	369
10	PFNA	463	419
11	9CL-PF3ONS	531	351
13	PFOS [e]	499	80
15	PFDA	513	469
17	NMeFOSAA [e]	570	419
19	NEtFOSAA [e]	584	419
20	11CL-PFOUdS	631	451
21	PFUnA	563	519
22	PFDoA	613	569
23	PFTrDA	663	619
24	PFTA	713	669
2	^{13}C-PFHxA	315	270
3	^{13}C-HFPO-DA	287	169
14	^{13}C-PFDA	515	470
16	d_5-NEtFOSAA	589	419
8	^{13}C-PFOA	415	370
12	^{13}C-PFOS	503	80
18	d_3-NMeFOSAA	573	419

[a] Segments are time durations in which single scan events occur; segments overlap where R.T. dictate.
[b] Precursor and product ions listed in this table are nominal masses. During MS and MS/MS optimization, the analyst should determine the precursor and product ion masses to one decimal place by locating the apex of the mass spectral peak place. These precursor and product ion masses (with one decimal place) should be used in the MS/MS method for all analyses.
[c] Ions used for quantitation purposes.
[d] Argon used as collision gas at a flow rate of 0.4 mL/min
[e] Analyte has multiple resolved chromatographic peaks due to linear and branched isomers. All peaks summed for quantitation purposes.

Determination of Selected Perfluorinated Alkyl Substances by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry Isotope Dilution (LC/MS/MS)

Reference: EPA Method 537, Version 1.1, September 2009, EPA Document #: EPA/600/R-08/09

EPA Method 537.1, Version 1, November 2018, EPA Document #: EPA/600/R-18/352

Department of Defense, Quality Systems Manual for Environmental Laboratories, Version 5.2, .2019

1. Scope and Application

Matrices: Drinking water, Non-potable Water, and Soil Matrices

Definitions: Refer to Alpha Analytical Quality Manual.

1.1 This is a liquid chromatography/tandem mass spectrometry (LC/MS/MS) method for the determination of selected perfluorinated alkyl substances (PFAS) in Non-Drinking Water and soil Matrices. Accuracy and precision data have been generated in reagent water, and finished ground and surface waters for the compounds listed in Table 1.

1.2 The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the operation of the LC/MS/MS and in the interpretation of LC/MS/MS data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

2.1 A 250-mL water sample is fortified with extracted internal standards (EIS) and passed through a solid phase extraction (WAX) cartridge containing a mixed mode, Weak Anion Exchange, reversed phase, water-wettable polymer to extract the method analytes and isotopically-labeled compounds. The compounds are eluted from the solid phase in two fractions with methanol followed by a small amount of 2% ammonium hydroxide in methanol solution. The extract is concentrated with nitrogen in a heated water bath, and then adjusted to a 1-mL volume with 80:20% (vol/vol) methanol:water. A 3 µl injection is made into an LC equipped with a C18 column that is interfaced to an MS/MS. The analytes are separated and identified by comparing the acquired mass spectra and retention times to reference spectra and retention times for calibration standards acquired under identical LC/MS/MS conditions. The concentration of each analyte is determined by using the isotope dilution technique. Extracted Internal Standards (EIS) analytes are used to monitor the extraction efficiency of the method analytes.

2.2 Method Modifications from Reference

None.

Table 1

Parameter	Acronym	CAS
PERFLUOROALKYL ETHER CARBOXYLIC ACIDS (PFECAs)		
Tetrafluoro-2-(heptafluoropropoxy)propanoic acid	HFPO-DA	62037-80-3
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4
PERFLUOROALKYLCARBOXILIC ACIDS (PFCAs)		
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	PFHxA *	307-24-4
Perfluoroheptanoic acid	PFHpA *	375-85-9
Perfluorooctanoic acid	PFOA *	335-67-1
Perfluorononanoic acid	PFNA *	375-95-1
Perfluorodecanoic acid	PFDA *	335-76-2
Perfluoroundecanoic acid	PFUnA *	2058-94-8
Perfluorododecanoic acid	PFDoA *	307-55-1
Perfluorotridecanoic acid	PFTrDA *	72629-94-8
Perfluorotetradecanoic acid	PFTA *	376-06-7
Perfluorohexadecanoic acid	PFHxDA	67905-19-5
Perfluorooctadecanoic acid	PFODA	16517-11-6
PERFLUOROALKYLSULFONATES (PFASs)		
Perfluorobutanesulfonic acid	PFBS *	375-73-5
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorohexanesulfonic acid	PFHxS *	355-46-4
Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorooctanesulfonic acid	PFOS *	1763-23-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluorododecanesulfonic acid	PFDoS	79780-39-5

*** also reportable via the standard 537 method**

Table 1 Cont.

Parameter	Acronym	CAS
CHLORO-PERFLUOROALKYLSULFONATE		
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9
9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid	9Cl-PF3ONS	756426-58-1
PERFLUOROOCTANESULFONAMIDES (FOSAs)		
Perfluorooctanesulfonamide	PFOSA	754-91-6
N-methylperfluoro-1-octanesulfonamide	NMeFOSA	31506-32-8
N-ethylperfluoro-1-octanesulfonamide	NEtFOSA	4151-50-2
TELOMER SULFONATES		
1H,1H,2H,2H-perfluorohexane sulfonate (4:2)	4:2FTS	27619-93-8
1H,1H,2H,2H-perfluorooctane sulfonate (6:2)	6:2FTS	27619-97-2
1H,1H,2H,2H-perfluorodecane sulfonate (8:2)	8:2FTS	39108-34-4
1H,1H,2H,2H-perfluorododecane sulfonate (10:2)	10:2FTS	120226-60-0
PERFLUOROOCTANESULFONAMIDOACETIC ACIDS		
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA *	2355-31-9
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA *	2991-50-6
NATIVE PERFLUOROOCTANESULFONAMIDOETHANOLS (FOSEs)		
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	NMeFOSE	24448-09-7
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	NEtFOSE	1691-99-2

*** also reportable via the standard 537 method**

3. Reporting Limits

The reporting limit for PFAS's is 2 ng/L for aqueous samples (20 ng/L for HFPO-DA) and 1 ng/g (10 ng/g for HFPO-DA) for soil samples.

4. Interferences

4.1 PFAS standards, extracts and samples should not come in contact with any glass containers or pipettes as these analytes can potentially adsorb to glass surfaces. PFAS analyte and EIS standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in polypropylene containers.

4.2 Method interferences may be caused by contaminants in solvents, reagents (including reagent water), sample bottles and caps, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. The method analytes in this method can also be found in many common laboratory supplies and equipment, such

as PTFE (polytetrafluoroethylene) products, LC solvent lines, methanol, aluminum foil, SPE sample transfer lines, etc. All items such as these must be routinely demonstrated to be free from interferences (less than 1/3 the RL for each method analyte) under the conditions of the analysis by analyzing laboratory reagent blanks as described in Section 9.2. **Subtracting blank values from sample results is not permitted.**

4.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature of the water. Humic and/or fulvic material can be co-extracted during SPE and high levels can cause enhancement and/or suppression in the electrospray ionization source or low recoveries on the SPE sorbent. Total organic carbon (TOC) is a good indicator of humic content of the sample.

4.4 SPE cartridges can be a source of interferences. The analysis of field and laboratory reagent blanks can provide important information regarding the presence or absence of such interferences. Brands and lots of SPE devices should be tested to ensure that contamination does not preclude analyte identification and quantitation.

5. Health and Safety

5.1 The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

5.2 All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.3 PFOA has been described as “likely to be carcinogenic to humans.” Pure standard materials and stock standard solutions of these method analytes should be handled with suitable protection to skin and eyes, and care should be taken not to breathe the vapors or ingest the materials.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection for Aqueous Samples

6.1.1 Samples must be collected in two (2) 250-mL high density polyethylene (HDPE) container with an unlined plastic screw cap.

6.1.2 The sample handler must wash their hands before sampling and wear nitrile gloves while filling and sealing the sample bottles. PFAS contamination during sampling can occur from a number of common sources, such as food packaging and certain foods and beverages. Proper hand washing and wearing nitrile gloves will aid in minimizing this type of accidental contamination of the samples.

6.1.3 Open the tap and allow the system to flush until the water temperature has stabilized (approximately 3 to 5 min). Collect samples from the flowing system.

6.1.4 Fill sample bottles. Samples do not need to be collected headspace free.

6.1.5 After collecting the sample and cap the bottle. Keep the sample sealed from time of collection until extraction.

6.1.6 Field Reagent Blank (FRB)

6.1.6.1 A FRB must be handled along with each sample set. The sample set is composed of samples collected from the same sample site and at the same time. At the laboratory, fill the field blank sample bottle with reagent water and preservatives, seal, and ship to the sampling site along with the sample bottles. For each FRB shipped, an empty sample bottle (no preservatives) must also be shipped. At the sampling site, the sampler must open the shipped FRB and pour the reagent water into the empty shipped sample bottle, seal and label this bottle as the FRB. The FRB is shipped back to the laboratory along with the samples and analyzed to ensure that PFAS's were not introduced into the sample during sample collection/handling.

The reagent water used for the FRBs must be initially analyzed for method analytes as a MB and must meet the MB criteria in Section 9.2.1 prior to use. This requirement will ensure samples are not being discarded due to contaminated reagent water rather than contamination during sampling.

6.2 Sample Collection for Soil and Sediment samples.

Grab samples are collected in polypropylene containers. Sample containers and contact surfaces containing PTFE shall be avoided.

6.3 Sample Preservation

Not applicable.

6.4 Sample Shipping

Samples must be chilled during shipment and must not exceed 10 °C during the first 48 hours after collection. Sample temperature must be confirmed to be at or below 10 °C when the samples are received at the laboratory. Samples stored in the lab must be held at or below 6 °C until extraction, but should not be frozen.

NOTE: Samples that are significantly above 10° C, at the time of collection, may need to be iced or refrigerated for a period of time, in order to chill them prior to shipping. This will allow them to be shipped with sufficient ice to meet the above requirements.

6.5 Sample Handling

6.5.1 Holding Times

6.5.1.1 Water samples should be extracted as soon as possible but must be extracted within 14 days. Soil samples should be extracted within 28 days. Extracts are stored at < 10 ° C and analyzed within 28 days after extraction.

7. Equipment and Supplies

7.1 SAMPLE CONTAINERS – 250-mL high density polyethylene (HDPE) bottles fitted with unlined screw caps. Sample bottles must be discarded after use.

7.2 POLYPROPYLENE BOTTLES – 4-mL narrow-mouth polypropylene bottles.

7.3 CENTRIFUGE TUBES – 50-mL conical polypropylene tubes with polypropylene screw caps for storing standard solutions and for collection of the extracts.

7.4 AUTOSAMPLER VIALS – Polypropylene 0.7-mL autosampler vials with polypropylene caps.

7.4.1 NOTE: Polypropylene vials and caps are necessary to prevent contamination of the sample from PTFE coated septa. However, polypropylene caps do not reseal, so evaporation occurs after injection. Thus, multiple injections from the same vial are not possible.

7.5 POLYPROPYLENE GRADUATED CYLINDERS – Suggested sizes include 25, 50, 100 and 1000-mL cylinders.

7.6 Auto Pipets – Suggested sizes include 5, 10, 25, 50, 100, 250, 500, 1000, 5000 and 10,000-µls.

7.7 PLASTIC PIPETS – Polypropylene or polyethylene disposable pipets.

7.8 ANALYTICAL BALANCE – Capable of weighing to the nearest 0.0001 g.

7.9 SOLID PHASE EXTRACTION (SPE) APPARATUS FOR USING CARTRIDGES

7.9.1 SPE CARTRIDGES – 0.5 g SPE cartridges containing a reverse phase copolymer characterized by a weak anion exchanger (WAX) sorbent phase.

7.9.2 VACUUM EXTRACTION MANIFOLD – A manual vacuum manifold with large volume sampler for cartridge extractions, or an automatic/robotic sample preparation system designed for use with SPE cartridges, may be used if all QC requirements discussed in Section 9 are met. Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system. Care must be taken with automated SPE systems to ensure the PTFE commonly used in these systems does not contribute to unacceptable analyte concentrations in the MB (Sect. 9.2.1).

7.9.3 SAMPLE DELIVERY SYSTEM – Use of a polypropylene transfer tube system, which transfers the sample directly from the sample container to the SPE cartridge, is recommended, but not mandatory. Standard extraction manifolds come equipped with PTFE transfer tube systems. These can be replaced with 1/8” O.D. x 1/16” I.D. polypropylene or polyethylene tubing cut to an appropriate length to ensure no sample contamination from the sample transfer lines. Other types of non-PTFE tubing may be used provided it meets the MB (Sect. 9.2.1) and LCS (Sect. 9.3) QC requirements. The PTFE transfer tubes may be used, but an MB must be run on each PFTE transfer tube and the QC requirements in Section 13.2.2 must be met. In the case of automated SPE, the removal of PTFE lines may not be feasible; therefore, MBs will need to be rotated among the ports and must meet the QC requirements of Sections 13.2.2 and 9.2.1.

7.10 Extract Clean-up Cartridge – 250 mg 6ml SPE Cartridge containing graphitized polymer carbon

7.11 EXTRACT CONCENTRATION SYSTEM – Extracts are concentrated by evaporation with nitrogen using a water bath set no higher than 65 °C.

7.12 LABORATORY OR ASPIRATOR VACUUM SYSTEM – Sufficient capacity to maintain a vacuum of approximately 10 to 15 inches of mercury for extraction cartridges.

7.13 LIQUID CHROMATOGRAPHY (LC)/TANDEM MASS SPECTROMETER (MS/MS) WITH DATA SYSTEM

7.13.1 LC SYSTEM – Instrument capable of reproducibly injecting up to 10-µL aliquots, and performing binary linear gradients at a constant flow rate near the flow rate used for development of this method (0.4 mL/min). The LC must be capable of pumping the water/methanol mobile phase without the use of a degasser which pulls vacuum on the mobile phase bottle (other types of degassers are acceptable). Degassers which pull vacuum on the mobile phase bottle will volatilize the ammonium acetate mobile phase causing the analyte peaks to shift to earlier retention times over the course of the analysis batch. The usage of a column heater is optional.

NOTE: During the course of method development, it was discovered that while idle for more than one day, PFAS's built up in the PTFE solvent transfer lines. To prevent long delays in purging high levels of PFAS's from the LC solvent lines, they were replaced with PEEK tubing and the PTFE solvent frits were replaced with stainless steel frits. It is not possible to remove all PFAS background contamination, but these measures help to minimize their background levels.

7.13.2 LC/TANDEM MASS SPECTROMETER – The LC/MS/MS must be capable of negative ion electrospray ionization (ESI) near the suggested LC flow rate of 0.4 mL/min. The system must be capable of performing MS/MS to produce unique product ions for the method analytes within specified retention time segments. A minimum of 10 scans across the chromatographic peak is required to ensure adequate precision.

7.13.3 DATA SYSTEM – An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should have the capability of processing stored LC/MS/MS data by recognizing an LC peak within any given retention time window. The software must allow integration of the ion abundance of any specific ion within specified time or scan number limits. The software must be able to calculate relative response factors, construct linear regressions or quadratic calibration curves, and calculate analyte concentrations.

7.13.4 ANALYTICAL COLUMN – An LC BEH C_{18} column (2.1 x 50 mm) packed with 1.7 µm d_p C_{18} solid phase particles was used. Any column that provides adequate resolution, peak shape, capacity, accuracy, and precision (Sect. 9) may be used.

8. Reagents and Standards

8.1 GASES, REAGENTS, AND SOLVENTS – Reagent grade or better chemicals should be used.

8.1.1 REAGENT WATER – Purified water which does not contain any measurable quantities of any method analytes or interfering compounds greater than 1/3 the RL for each method analyte of interest. Prior to daily use, at least 3 L of reagent water should be flushed from the purification system to rinse out any build-up of analytes in the system's tubing.

8.1.2 METHANOL (CH_3OH, CAS#: 67-56-1) – High purity, demonstrated to be free of analytes and interferences.

8.1.3 AMMONIUM ACETATE ($NH_4C_2H_3O_2$, CAS#: 631-61-8) – High purity, demonstrated to be free of analytes and interferences.

8.1.4 ACETIC ACID (H_3CCOOH, CAS#: 64-19-7) - High purity, demonstrated to be free of analytes and interferences.

8.1.5 1M AMMONIUM ACETATE/REAGENT WATER – High purity, demonstrated to be free of analytes and interferences.

8.1.6 2mM AMMONIUM ACETATE/METHANOL:WATER (5:95) – To prepare, mix 2 ml of 1M AMMONIUM ACETATE,1 ml ACETIC ACID and 50 ml METHANOL into l Liter of REAGENT WATER.

8.1.7 Methanol/Water (80:20) – To prepare a 1 Liter bottle, mix 200 ml of REAGENT WATER with 800 ml of METHANOL.

8.1.8 AMMONIUM HYDROXIDE (NH_3, CAS#: 1336-21-6) – High purity, demonstrated to be free of analytes and interferences.

8.1.9 Sodium Acetate ($NaOOCCH_3$, CAS#: 127-09-3) – High purity, demonstrated to be free of analytes and interferences.

8.1.10 25 mM Sodium Acetate Buffer – To prepare 250mls, dissolve .625 grams of sodium acetate into 100 mls of reagent water. Add 4 mls Acetic Acid and adjust the final volume to 250 mls with reagent water.

8.1.11 NITROGEN – Used for the following purposes: Nitrogen aids in aerosol generation of the ESI liquid spray and is used as collision gas in some MS/MS instruments. The nitrogen used should meet or exceed instrument manufacturer's specifications. In addition, Nitrogen is used to concentrate sample extracts (Ultra High Purity or equivalent).

8.1.12 ARGON – Used as collision gas in MS/MS instruments. Argon should meet or exceed instrument manufacturer's specifications. Nitrogen gas may be used as the collision gas provided sufficient sensitivity (product ion formation) is achieved.

8.2 STANDARD SOLUTIONS – When a compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. PFAS analyte and IS standards commercially purchased in glass ampoules are acceptable; however, all subsequent transfers or dilutions performed by the analyst must be prepared and stored in polypropylene containers. Standards for sample fortification generally should be prepared in the smallest volume that can be accurately measured to minimize the addition of excess organic solvent to aqueous samples.

NOTE: Stock standards and diluted stock standards are stored at ≤4 °C.

8.2.1 ISOTOPE DILUTION Extracted Internal Standard (ID EIS) STOCK SOLUTIONS - ID EIS stock standard solutions are stable for at least 6 months when stored at 4 °C. The stock solution is purchased at a concentration of 1000 ng/mL.

8.2.2 ISOTOPE DILUTION Extracted Internal Standard PRIMARY DILUTION STANDARD (ID EIS PDS) – Prepare the ID EIS PDS at a concentration of 500 ng/mL. The ID PDS is prepared in 80:20% (vol/vol) methanol:water. The ID PDS is stable for 6 months when stored at ≤4 °C.

Table 2

Isotope Labeled Standard	Conc. of EIS Stock (ng/mL)	Vol. of EIS Stock (mL)	Final Vol. of EIS PDS (mL)	Final Conc. of EIS PDS (ng/mL)
M4PFBA	1000	1.0	2.0	500
M5PFPeA	1000	1.0	2.0	500
M5PFHxA	1000	1.0	2.0	500
M4PFHpA	1000	1.0	2.0	500
M8PFOA	1000	1.0	2.0	500
M9PFNA	1000	1.0	2.0	500
M6PFDA	1000	1.0	2.0	500
M7PFUdA	1000	1.0	2.0	500
MPFDoA	1000	1.0	2.0	500
M2PFTeDA	1000	1.0	2.0	500
M2PFHxDA	50,000	.02	2.0	500
d3-N-MeFOSA	50,000	.02	2.0	500
d5-N-EtFOSA	50,000	.02	2.0	500
d7-N-MeFOSE	50,000	.02	2.0	500
d9-N-EtFOSE	50,000	.02	2.0	500
M8FOSA	1000	1.0	2.0	500
d3-N-MeFOSAA	1000	1.0	2.0	500
d5-N-EtFOSAA	1000	1.0	2.0	500
M3PFBS	929	1.0	2.0	464.5
M3PFHxS	946	1.0	2.0	473
M8PFOS	957	1.0	2.0	478.5
M2-4:2FTS	935	1.0	2.0	467.5
M2-6:2FTS	949	1.0	2.0	474.5
M2-8:2FTS	958	1.0	2.0	479
M3HFPO-DA	50,000	.4	2.0	10,000

8.2.3 ANALYTE STOCK STANDARD SOLUTION – Analyte stock standards are stable for at least 6 months when stored at 4 °C. When using these stock standards to prepare a PDS, care must be taken to ensure that these standards are at room temperature and adequately vortexed.

8.2.4 Analyte Secondary Spiking Standard Prepare the spiking solution of additional add on components for project specific requirements only. ANALYTE PRIMARY SPIKING STANDARD – Prepare the spiking standard at a concentration of 500 ng/mL in methanol. The spiking standard is stable for at least two months when stored in polypropylene centrifuge tubes at room temperature.

Table 3

Analyte	Conc. of IS Stock (ng/mL)	Vol. of IS Stock (mL)	Final Vol. of IS PDS (mL)	Final Conc. of IS PDS (ng/mL)
PFBA	2000	1	4	500
PFPeA	2000	1	4	500
PFHxA	2000	1	4	500
PFHpA	2000	1	4	500
PFOA	2000	1	4	500
PFNA	2000	1	4	500
PFDA	2000	1	4	500
PFUdA	2000	1	4	500
PFDoA	2000	1	4	500
PFTrDA	2000	1	4	500
PFTeDA	2000	1	4	500
FOSA	2000	1	4	500
N-MeFOSAA	2000	1	4	500
N-EtFOSAA	2000	1	4	500
L-PFBS	1770	1	4	442.5
L-PFPeS	1880	1	4	470
L-PFHxSK	1480	1	4	370
Br-PFHxSK	344	1	4	86
L-PFHpS	1900	1	4	475
L-PFOSK	1460	1	4	365
Br-PFOSK	391	1	4	97.75
L-PFNS	1920	1	4	480
L-PFDS	1930	1	4	482.5
4:2FTS	1870	1	4	467.5
6:2FTS	1900	1	4	475
8:2FTS	1920	1	4	480

8.2.5 Analyte Secondary Spiking Standard Prepare the spiking solution of additional add on components for project specific requirements only.

Table 4

Analyte	Conc. of IS Stock (ng/mL)	Vol. of IS Stock (mL)	Final Vol. of IS PDS (mL)	Final Conc. of IS PDS (ng/mL)
ADONA	2000	1	4	500
PFHxDA	2000	1	4	500
PFODA	2000	1	4	500
HFPO-DA	100,000	.4	4	10,000
9ClPF3ONS	50,000	0.04	4	500
11ClPF3OUdS	50,000	0.04	4	500

8.2.6 LOW, MEDIUM AND HIGH LEVEL LCS – The LCS's will be prepared at the following concentrations and rotated per batch; 2 ng/L, 40 ng/L, 500 ng/l for drinking waters. The analyte PDS contains all the method analytes of interest at various concentrations in methanol. The analyte PDS has been shown to be stable for six months when stored at ≤4 °C.

8.2.7 Isotope Dilution Labeled Recovery Stock Solutions (ID REC) – ID REC Stock solutions are stable for at least 6 months when stored at 4 °C. The stock solution is purchased at a concentration of 1000 ng/mL.

8.2.8 Isotope Dilution Labeled Recovery Primary Dilution Standard (ID REC PDS) - Prepare the ID REC PDS at a concentration of 500 ng/mL. The ID REC PDS is prepared in 80:20% (vol/vol) methanol:water. The ID REC PDS is stable for at least six months when stored in polypropylene centrifuge tubes at ≤4 °C.

Table 5

Analyte	Conc. of REC Stock (ng/mL)	Vol. of REC Stock (mL)	Final Vol. of REC PDS (mL)	Final Conc. of REC PDS (ng/mL)
M2PFOA	2000	1	4	500
M2PFDA	2000	1	4	500
M3PFBA	2000	1	4	500
M4PFOS	2000	1	4	500

8.2.9 CALIBRATION STANDARDS (CAL) –

Current Concentrations (ng/mL): 0.5, 1.0, 5.0, 10.0, 50.0, 125, 150, 250, 500

Prepare the CAL standards over the concentration range of interest from dilutions of the analyte PDS in methanol containing 20% reagent water. 20 µl of the EIS PDS and REC PDS are added to the CAL standards to give a constant concentration of 10 ng/ml. The lowest concentration CAL standard must be at or below the RL (2 ng/L), which may depend on system sensitivity. The CAL standards may also be used as CCVs (Sect. 9.8). To make calibration stock standards:

Table 6

Calibration Standard Concentration	Final Aqueous Cal STD Level Concentration	Final Soil Cal STD Level Concentration	24 compound stock added (ul)	PFHxDA Stock added (ul)	500 ng/ml PFHxDA dilution added (ul)	PFODA Stock added (ul)	500 ng/ml PFODA dilution added (ul)	ADONA, HFPO-DA, 11Cl-PF3OUdS, 9Cl-PF3ONS Stock added (ul)	500 ng/ml ADONA dilution added (ul)	Final Volume in MeOH/H_2O (82:20)
.5 ng/ml	2 ng/L	.25 ng/g	6.25		25		25		25	25 mls
1 ng/ml	4 ng/L	.5 ng/g	5		20		20		20	10 mls
5 ng/ml	20 ng/L	1 ng/g	25		100		100		100	10 mls
10 ng/ml	40 ng/L	5 ng/g	125	5		5		5		25 mls

50 ng/ml	200 ng/L	25 ng/g	250	10		10		10		10 mls
125 ng/ml	500 ng/L	62.5 ng/g	625	25		25		25		10 mls
150 ng/ml	600 ng/L	75 ng/g	750	30		30		30		10 mls
250 ng/ml	1000 ng/L	125 ng/g	625							5 mls
500 ng/ml	2000 ng/L	250 ng/g	1250							5 mls

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 MINIMUM REPORTING LIMIT (MRL) CONFIRMATION

9.1.1 Fortify, extract, and analyze seven replicate LCSs at 2 ng/l. Calculate the mean measured concentration (*Mean*) and standard deviation for these replicates. Determine the Half Range for the prediction interval of results (HR_{PIR}) using the equation below

$$HR_{PIR} = 3.963s$$

Where:

s = the standard deviation
3.963 = a constant value for seven replicates.

9.1.2 Confirm that the upper and lower limits for the Prediction Interval of Result (*PIR* = *Mean* ± HR_{PIR}) meet the upper and lower recovery limits as shown below

The Upper PIR Limit must be ≤150% recovery.

$$\frac{Mean + HR_{PIR}}{Fortified\ Concentration} \times 100\% \leq 150\%$$

The Lower PIR Limit must be ≥ 50% recovery.

$$\frac{Mean - HR_{PIR}}{Fortified\ Concentration} \times 100\% \geq 50\%$$

9.1.3 The RL is validated if both the Upper and Lower PIR Limits meet the criteria described above. If these criteria are not met, the RL has been set too low and must be determined again at a higher concentration.

9.2 Blank(s)

9.2.1 **METHOD BLANK (MB) -** A Method Blank (MB) is required with each extraction batch to confirm that potential background contaminants are not interfering with the identification or quantitation of method analytes. Prep and analyze a MB for every 20 samples. If the MB produces a peak within the retention time window of any analyte that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples. Background contamination must be reduced to an acceptable level before proceeding. Background from method analytes or other contaminants that

interfere with the measurement of method analytes must be below the RL. If the method analytes are detected in the MB at concentrations equal to or greater than this level, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch. Because background contamination is a significant problem for several method analytes, it is highly recommended that the analyst maintain a historical record of MB data.

9.2.2 **FIELD REAGENT BLANK (FRB)** - The purpose of the FRB is to ensure that PFAS's measured in the Field Samples were not inadvertently introduced into the sample during sample collection/handling. Analysis of the FRB is required only if a Field Sample contains a method analyte or analytes at or above the RL. The FRB is processed, extracted and analyzed in exactly the same manner as a Field Sample.

9.3 Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicates (LCSD)

9.3.1 An LCS is required with each extraction batch. The fortified concentration of the LCS may be rotated between low, medium, and high concentrations from batch to batch. Default limits of 50-150% of the true value may be used for analytes until sufficient replicates have been analyzed to generate proper control limits. Calculate the percent recovery (%*R*) for each analyte using the equation

$$\%R = \frac{A \times 100}{B}$$

Where:

A = measured concentration in the fortified sample
B =fortification concentration.

9.3.2 Where applicable, LCSD's are to be extracted and analyzed. The concentration and analyte recovery criteria for the LCSD must be the same as the batch LCS The RSD's must fall within ≤30% of the true value for medium and high level replicates, and ≤50% for low level replicates. Calculate the relative percent difference (RPD) for duplicate MSs (MS and MSD) using the equation

$$RPD = \frac{|LCS - LCSD|}{(LCS + LCSD) / 2} \times 100$$

9.3.3 **If the LCS and or LCSD results do not meet these criteria for method analytes, then all data for the problem analyte(s) must be considered invalid for all samples in the extraction batch.**

9.4 Labeled Recovery Standards (REC)

The analyst must monitor the peak areas of the REC(s) in all injections during each analysis day.

9.5 Extracted Internal Standards (EIS)

9.5.1 The EIS standard is fortified into all samples, CCVs, MBs, LCSs, MSs, MSDs, FD, and FRB prior to extraction. It is also added to the CAL standards. The EIS is a means of assessing method performance from extraction to final

chromatographic measurement. Calculate the recovery (%R) for the EIS using the following equation

$$\%R = (A / B) \times 100$$

Where:

A = calculated EIS concentration for the QC or Field Sample
B = fortified concentration of the EIS.

9.5.2 Default limits of 50-150% may be used for analytes until sufficient replicates have been analyzed to generate proper control limits. A low or high percent recovery for a sample, blank, or CCV does not require discarding the analytical data but it may indicate a potential problem with future analytical data. When EIS recovery from a sample, blank, or CCV are outside control limits, check 1) calculations to locate possible errors, 2) standard solutions for degradation, 3) contamination, and 4) instrument performance. For CCVs and QC elements spiked with all target analytes, if the recovery of the corresponding target analytes meet the acceptance criteria for the EIS in question, the data can be used but all potential biases in the recovery of the EIS must be documented in the sample report. If the associated target analytes do not meet the acceptance criteria,the data must be reanalyzed.

9.6 Matrix Spike (MS)

9.6.1 Analysis of an MS is required in each extraction batch and is used to determine that the sample matrix does not adversely affect method accuracy. Assessment of method precision is accomplished by analysis of a Field Duplicate (FD) (Sect. 9.6); however, infrequent occurrence of method analytes would hinder this assessment. If the occurrence of method analytes in the samples is infrequent, or if historical trends are unavailable, a second MS, or MSD, must be prepared, extracted, and analyzed from a duplicate of the Field Sample. Extraction batches that contain MSDs will not require the extraction of a field sample duplicate. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, method performance should be established for each. Over time, MS data should be documented by the laboratory for all routine sample sources.

9.6.2 Within each extraction batch, a minimum of one Field Sample is fortified as an MS for every 20 Field Samples analyzed. The MS is prepared by spiking a sample with an appropriate amount of the Analyte Stock Standard (Sect. 8.2.3). Use historical data and rotate through the low, mid and high concentrations when selecting a fortifying concentration. Calculate the percent recovery (%*R*) for each analyte using the equation

$$\%R = \frac{(A - B)}{C} \times 100$$

Where:

A = measured concentration in the fortified sample
B = measured concentration in the unfortified sample
C = fortification concentration.

9.6.3 Analyte recoveries may exhibit matrix bias. For samples fortified at or above their native concentration, recoveries should range between 50-150%. If the accuracy of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the LCS, the recovery is judged to be

matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.7 Laboratory Duplicate

9.7.1 FIELD DUPLICATE OR LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (FD or MSD) – Within each extraction batch (not to exceed 20 Field Samples), a minimum of one FD or MSD must be analyzed. Duplicates check the precision associated with sample collection, preservation, storage, and laboratory procedures. If method analytes are not routinely observed in Field Samples, an MSD should be analyzed rather than an FD.

9.7.2 Calculate the relative percent difference (*RPD*) for duplicate measurements (*FD1* and *FD2*) using the equation

$$RPD = \frac{|FD1 - FD2|}{(FD1 + FD2) / 2} \times 100$$

9.7.3 RPDs for FDs should be ≤30%. Greater variability may be observed when FDs have analyte concentrations that are within a factor of 2 of the RL. At these concentrations, FDs should have RPDs that are ≤50%. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the CCV, the recovery is judged to be matrix biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.7.4 If an MSD is analyzed instead of a FD, calculate the relative percent difference (RPD) for duplicate MSs (MS and MSD) using the equation

$$RPD = \frac{|MS - MSD|}{(MS + MSD) / 2} \times 100$$

9.7.5 RPDs for duplicate MSs should be ≤30% for samples fortified at or above their native concentration. Greater variability may be observed when MSs are fortified at analyte concentrations that are within a factor of 2 of the RL. MSs fortified at these concentrations should have RPDs that are ≤50% for samples fortified at or above their native concentration. If the RPD of any analyte falls outside the designated range, and the laboratory performance for that analyte is shown to be in control in the LCSD where applicable, the result is judged to be matrix biased. If no LCSD is present, the associated MS and MSD are to be re-analyzed to determine if any analytical has occurred. If the resulting RPDs are still outside control limits, the result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

9.8 Initial Calibration Verification (ICV)

9.8.1 As part of the IDC (Sect. 13.2), and after each ICAL, analyze a QCS sample from a source different from the source of the CAL standards. If a second vendor is not available, then a different lot of the standard should be used. The QCS should be prepared and analyzed just like a CCV. Acceptance criteria for the QCS are identical to the CCVs; the calculated amount for each analyte must be ±

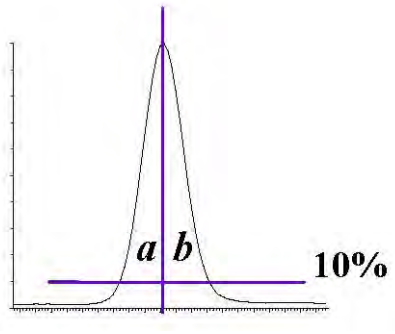
30% of the expected value. If measured analyte concentrations are not of acceptable accuracy, check the entire analytical procedureto locate and correct the problem.

9.9 Continuing Calibration Verification (CCV)

9.9.1 CCV Standards are analyzed at the beginning of each analysis batch, after every 10 Field Samples, and at the end of the analysis batch. See Section 10.7 for concentration requirements and acceptance criteria.

9.10 Method-specific Quality Control Samples

9.10.1 PEAK ASYMMETRY FACTOR – A peak asymmetry factor must be calculated using the equation below during the IDL and every time a calibration curve is generated. The peak asymmetry factor for the first two eluting peaks in a midlevel CAL standard (if only two analytes are being analyzed, both must be evaluated) must fall in the range of 0.8 to 1.5. Modifying the standard or extract composition to more aqueous content to prevent poor shape is not permitted. See guidance in Section 10.6.4.1 if the calculated peak asymmetry factors do not meet the criteria.



$$A_s = b / a$$

Where:

A_s = peak asymmetry factor
b = width of the back half of the peak measured (at 10% peak height) from the trailing edge of the peak to a line dropped perpendicularly from the peak apex
a = the width of the front half of the peak measured (at 10% peak height) from the leading edge of the peak to a line dropped perpendicularly from the apex.

9.11 Method Sequence

- CCV-LOW
- MB
- LCS
- LCSD
- MS
- Duplicate or MSD
- Field Samples (1-10)
- CCV-MID
- Field Samples (11-20)
- CCV-LOW

10. Procedure

10.1 Equipment Set-up

10.1.1 This procedure may be performed manually or in an automated mode using a robotic or automatic sample preparation device. If an automated system is used to prepare samples, follow the manufacturer's operating instructions, but all extraction and elution steps must be the same as in the manual procedure. Extraction and/or elution steps may not be changed or omitted to accommodate the use of an automated system. If an automated system is used, the MBs should be rotated among the ports to ensure that all the valves and tubing meet the MB requirements (Sect. 9.2).

10.1.2 Some of the PFAS's adsorb to surfaces, including polypropylene. Therefore, the aqueous sample bottles must be rinsed with the elution solvent (Sect 10.3.4) whether extractions are performed manually or by automation. The bottle rinse is passed through the cartridge to elute the method analytes and is then collected (Sect. 10.3.4).

10.1.3 **NOTE:** The SPE cartridges and sample bottles described in this section are designed as single use items and should be discarded after use. They may not be refurbished for reuse in subsequent analyses.

10.2 Sample Preparation and Extraction of Aqueous Samples

10.2.1 Samples are preserved, collected and stored as presented in Section 6.

The entire sample that is received must be sent through the SPE cartridge. In addition, the bottle must be solvent rinsed and this rinse must be sent through the SPE cartridge as well. The method blank (MB) and laboratory control sample (LCS) must be extracted in exactly the same manner (i.e., must include the bottle solvent rinse). It should be noted that a water rinse alone is not sufficient. This does not apply to samples with high concentrations of PFAS that are prepared using serial dilution and not SPE.

10.2.2 Determine sample volume. Weigh all samples to the nearest 1g. If visible sediment is present, centrifuge and decant into a new 250mL HDPE bottle and record the weight of the new container.

NOTE: Some of the PFAS's adsorb to surfaces, thus the sample volume may **NOT** be transferred to a graduated cylinder for volume measurement.

10.2.3 The MB, LCS and FRB may be prepared by measuring 250 mL of reagent water with a polypropylene graduated cylinder or filling a 250-mL sample bottle to near the top.

10.2.4 Adjust the QC and sample pH to 3 by adding acetic acid in water dropwise

10.2.5 Add 20 µL of the EIS PDS (Sect. 8.2.2) to each sample and QC, cap and invert to mix.

10.2.6 If the sample is an LCS, LCSD, MS, or MSD, add the necessary amount of analyte PDS (Sect. 8.2.3). Cap and invert each sample to mix.

10.3 Cartridge SPE Procedure

10.3.1 CARTRIDGE CLEAN-UP AND CONDITIONING – DO NOT allow cartridge packing material to go dry during any of the conditioning steps. Rinse each cartridge with 3 X 5 mL of 2% ammonium hydroxide in methanol, followed by 5mls of methanol. Next, rinse each cartridge with 5 mls of the 25 mM acetate buffer, followed by 15 mL of reagent water, without allowing the water to drop below the top edge of the packing. If the cartridge goes dry during the conditioning phase, the conditioning must be started over. Add 4-5 mL of reagent water to each cartridge, attach the sample transfer tubes (Sect. 7.9.3), turn on the vacuum, and begin adding sample to the cartridge.

10.3.2 SAMPLE EXTRACTON – Adjust the vacuum so that the approximate flow rate is approximately 4 mL/min. Do not allow the cartridge to go dry before all the sample has passed through.

10.3.3 SAMPLE BOTTLE AND CARTRIDGE RINSE – After the entire sample has passed through the cartridge, rinse the sample bottles with 4 ml reagent water followed by 4 ml 25 mM acetate buffer at pH 4 and draw the aliquot through the sample transfer tubes and the cartridges. Draw air or nitrogen through the cartridge for 5-10 min at high vacuum (10-15 in. Hg). **NOTE: If empty plastic reservoirs are used in place of the sample transfer tubes to pass the samples through the cartridges, these reservoirs must be treated like the transfer tubes. After the entire sample has passed through the cartridge, the reservoirs must be rinsed to waste with reagent water.**

10.3.4 SAMPLE BOTTLE AND CARTRIDGE ELUTION, Fraction 1 – Turn off and release the vacuum. Lift the extraction manifold top and insert a rack with collection tubes into the extraction tank to collect the extracts as they are eluted from the cartridges. Rinse the sample bottles with 12 mls of methanol and draw the aliquot through the sample transfer tubes and cartridges. Use a low vacuum such that the solvent exits the cartridge in a dropwise fashion.

SAMPLE BOTTLE AND CARTRIDGE ELUTION, Fraction 2 In a separate collection vial, rinse the sample bottles with 12 mL of 2% ammonium hydroxide in methanol and elute the analytes from the cartridges by pulling the 4 mL of methanol through the sample transfer tubes and the cartridges. Use a low vacuum such that the solvent exits the cartridge in a dropwise fashion. To the final extract, add 50 ul of acetic acid.

NOTE: If empty plastic reservoirs are used in place of the sample transfer tubes to pass the samples through the cartridges, these reservoirs must be treated like the transfer tubes. After the reservoirs have been rinsed in Section 10.3.3, the elution solvent used to rinse the sample bottles must be swirled down the sides of the reservoirs while eluting the cartridge to ensure that any method analytes on the surface of the reservoirs are transferred to the extract.

CLEAN-UP CARTRIDGE ELUTION, Elute the clean-up cartridge with 8 additional mls of methanol and draw the aliquot through the cartridge. Use a low vacuum such that the solvent exits the cartridge in a dropwise fashion.

10.3.5 Fractions 1 and 2 are to be combined during the concentration stage (section10.6)

10.4 Sample Prep and Extraction Protocol for Soils

10.4.1 Homogenize and weigh 2 grams of sample (measured to the nearest hundredth of a gram) intoa 50 ml polypropylene centrifuge tube. For laboratory control blanks and spikes, 2 grams of clean sand is used.

10.4.2 Add 20 µL of the EIS PDS (Sect. 8.2.2) to each sample and QC.

10.4.3 If the sample is an LCS, LCSD, MS, or MSD, add the necessary amount of analyte PDS (Sect. 8.2.3). Cap and invert each sample to mix.

10.4.4 To all samples, add 10 mls of methanol, cap, vortex for 25 seconds at 3000RPM and mix for 30 minutes using a shaker table of tumbler at 120RPM.

10.4.5 Following mixing, sonicate each sample for 30 minutes and let samples sit overnight (at least 2 hours is required for RUSH samples).

10.4.6 Centrifuge each sample at 3500RPM for 10 minutes.

10.4.7 Remove supernatant, and reserve for clean-up.

10.5 Extract Clean-up

10.5.1 CARTRIDGE CLEAN-UP AND CONDITIONING –. Rinse each cartridge with 15 mL of methanol and discard. If the cartridge goes dry during the conditioning phase, the conditioning must be started over. Attach the sample transfer tubes (Sect. 7.9.3), turn on the vacuum, and begin adding sample to the cartridge.

10.5.2 Adjust the vacuum so that the approximate flow rate is 1-2 mL/min. Do not allow the cartridge to go dry before all the sample has passed through.

10.5.3 SAMPLE BOTTLE AND CARTRIDGE RINSE – After the entire sample has passed through the cartridge, rinse the sample collection vial with two 1-mL aliquots of methanol and draw each aliquot through the cartridges. Draw air or nitrogen through the cartridge for 5 min at high vacuum (10-15 in. Hg).

10.5.4 If extracts are not to be immediately evaporated, cover collection tubes and store at ambient temperature till concentration.

10.6 Extract Concentration

10.6.1 Concentrate the extract to dryness under a gentle stream of nitrogen in a heated water bath (60-65 °C) to remove all the water/methanol mix. Add the appropriate amount of 80:20% (vol/vol) methanol:water solution and 20 µl of the ID REC PDS (Sect. 8.2.7) to the collection vial to bring the volume to 1 mL and vortex. Transfer two aliquots with a plastic pipet (Sect. 7.6) into 2 polypropylene autosampler vials.

NOTE: It is recommended that the entire 1-mL aliquot not be transferred to the autosampler vial because the polypropylene autosampler caps do not reseal after injection. Therefore, do not store the extracts in the autosampler vials as evaporation losses can occur occasionally in these autosampler vials. Extracts can be split between 2 X 700 µl vials (Sect. 7.4).

10.7 Sample Volume Determination

10.7.1 If the level of the sample was marked on the sample bottle, use a graduated cylinder to measure the volume of water required to fill the original sample bottle to the mark made prior to extraction. Determine to the nearest 10 mL.

10.7.2 If using weight to determine volume, weigh the empty bottle to the nearest 10 g and determine the sample weight by subtraction of the empty bottle weight from the original sample weight (Sect. 10.2.2). Assume a sample density of 1.0 g/mL. In either case, the sample volume will be used in the final calculations of the analyte concentration (Sect. 11.2).

10.8 Initial Calibration - Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed. After the initial calibration is successful, a CCV is required at the beginning and end of each period in which analyses are performed, and after every tenth Field Sample.

10.8.1 ESI-MS/MS TUNE

10.8.1.1 Calibrate the mass scale of the MS with the calibration compounds and procedures prescribed by the manufacturer.

10.8.1.2 Optimize the [M-H]- for each method analyte by infusing approximately 0.5-1.0 µg/mL of each analyte (prepared in the initial mobile phase conditions) directly into the MS at the chosen LC mobile phase flow rate (approximately 0.4 mL/min). This tune can be done on a mix of the method analytes. The MS parameters (voltages, temperatures, gas flows, etc.) are varied until optimal analyte responses are determined. The method analytes may have different optima requiring some compromise between the optima.

10.8.1.3 Optimize the product ion for each analyte by infusing approximately 0.5-1.0 µg/mL of each analyte (prepared in the initial mobile phase conditions) directly into the MS at the chosen LC mobile phase flow rate (approximately 0.4 mL/min). This tune can be done on a mix of the method analytes. The MS/MS parameters (collision gas pressure, collision energy, etc.) are varied until optimal analyte responses are determined. Typically, the carboxylic acids have very similar MS/MS conditions and the sulfonic acids have similar MS/MS conditions.

10.8.2 Establish LC operating parameters that optimize resolution and peak shape. Modifying the standard or extract composition to more aqueous content to prevent poor shape is not permitted.

Cautions: LC system components, as well as the mobile phase constituents, contain many of the method analytes in this method. Thus, these PFAS's will build up on the head of the LC column during mobile phase equilibration. To minimize the background PFAS peaks and to keep background levels constant, the time the LC column sits at initial conditions must be kept constant and as short as possible (while ensuring reproducible retention times). In addition, prior to daily use, flush the column with 100% methanol for at least 20 min before initiating a sequence. It may be necessary on some systems to flush other LC components such as wash syringes, sample needles or any other system components before daily use.

10.8.3 Inject a mid-level CAL standard under LC/MS conditions to obtain the retention times of each method analyte. If analyzing for PFTA, ensure that the LC

conditions are adequate to prevent co-elution of PFTA and the mobile phase interferants. These interferants have the same precursor and products ions as PFTA, and under faster LC conditions may co-elute with PFTA. Divide the chromatogram into retention time windows each of which contains one or more chromatographic peaks. During MS/MS analysis, fragment a small number of selected precursor ions ([M-H]-) for the analytes in each window and choose the most abundant product ion. For maximum sensitivity, small mass windows of ±0.5 daltons around the product ion mass were used for quantitation.

10.8.4 Inject a mid-level CAL standard under optimized LC/MS/MS conditions to ensure that each method analyte is observed in its MS/MS window and that there are at least 10 scans across the peak for optimum precision.

10.8.4.1 If broad, split or fronting peaks are observed for the first two eluting chromatographic peaks (if only two analytes are being analyzed, both must be evaluated), change the initial mobile phase conditions to higher aqueous content until the peak asymmetry ratio for each peak is 0.8 – 1.5. The peak asymmetry factor is calculated as described in Section 9.9.1 on a mid-level CAL standard. The peak asymmetry factor must meet the above criteria for the first two eluting peaks during the IDL and every time a new calibration curve is generated. Modifying the standard or extract composition to more aqueous content to prevent poor shape is not permitted.

NOTE: PFHxS, PFOS, NMeFOSAA, and NEtFOSAA have multiple chromatographic peaks using the LC conditions in Table 5 due to chromatographic resolution of the linear and branched isomers of these compounds. Most PFAS's are produced by two different processes. One process gives rise to linear PFAS's only while the other process produces both linear and branched isomers. Thus, both branched and linear PFAS's can potentially be found in the environment. For the aforementioned compounds that give rise to more than one peak, all the chromatographic peaks observed in the standard must be integrated and the areas totaled. Chromatographic peaks in a sample must be integrated in the same way as the CAL standard.

10.8.5 Prepare a set of CAL standards as described in Section 8.2.5. The lowest concentration CAL standard must be at or below the RL (2 ng/L), which may depend on system sensitivity.

10.8.6 The LC/MS/MS system is calibrated using the IS technique. Use the LC/MS/MS data system software to generate a linear regression or quadratic calibration curve for each of the analytes. This curve **must always** be forced through zero and may be concentration weighted, if necessary. Forcing zero allows for a better estimate of the background levels of method analytes. A minimum of 5 levels are required for a linear calibration model and a minimum of 6 levels are required for a quadratic calibration model.

10.8.7 CALIBRATION ACCEPTANCE CRITERIA – A linear fit is acceptable if the coefficient of determination (r^2) is greater than 0.99. When quantitated using the initial calibration curve, each calibration point, except the lowest point, for each analyte should calculate to be within 70-130% of its true value. The lowest CAL point should calculate to be within 50-150% of its true value. If these criteria cannot be met, the analyst will have difficulty meeting ongoing QC criteria. It is

recommended that corrective action is taken to reanalyze the CAL standards, restrict the range of calibration, or select an alternate method of calibration (forcing the curve through zero is still required).

10.8.7.1 CAUTION: When acquiring MS/MS data, LC operating conditions must be carefully reproduced for each analysis to provide reproducible retention times. If this is not done, the correct ions will not be monitored at the appropriate times. As a precautionary measure, the chromatographic peaks in each window must not elute too close to the edge of the segment time window.

10.9 CONTINUING CALIBRATION CHECK (CCV) – Minimum daily calibration verification is as follows. Verify the initial calibration at the beginning and end of each group of analyses, and after every tenth sample during analyses. In this context, a "sample" is considered to be a Field Sample. MBs, CCVs, LCSs, MSs, FDs FRBs and MSDs are not counted as samples. The beginning CCV of each analysis batch must be at or below the RL in order to verify instrument sensitivity prior to any analyses. If standards have been prepared such that all low CAL points are not in the same CAL solution, it may be necessary to analyze two CAL standards to meet this requirement. Alternatively, the analyte concentrations in the analyte PDS may be customized to meet these criteria. Subsequent CCVs should alternate between a medium and Low concentration CAL standard.

10.9.1 Inject an aliquot of the appropriate concentration CAL standard and analyze with the same conditions used during the initial calibration.

10.9.2 Calculate the concentration of each analyte and EIS in the CCV. The calculated amount for each analyte for medium level CCVs must be within ± 30% of the true value with an allowance of 10% of the reported analytes to be greater than 30%, but less than 40%. The calculated amount for each EIS must be within ± 50% of the true value. The calculated amount for the lowest calibration point for each analyte must be within ± 50%. If these conditions do not exist, then all data for the problem analyte must be considered invalid, and remedial action should be taken (Sect. 10.7.4) which may require recalibration. Any Field or QC Samples that have been analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored, with the following exception. **If the CCV fails because the calculated concentration is greater than 130% (150% for the low-level CCV) for a particular method analyte, and Field Sample extracts show no detection for that method analyte, non-detects may be reported without re-analysis.**

10.9.3 REMEDIAL ACTION – Failure to meet CCV QC performance criteria may require remedial action. Major maintenance, such as cleaning the electrospray probe, atmospheric pressure ionization source, cleaning the mass analyzer, replacing the LC column, etc., requires recalibration (Sect 10.6) and verification of sensitivity by analyzing a CCV at or below the RL (Sect 10.7).

10.10 EXTRACT ANALYSIS

10.10.1 Establish operating conditions equivalent to those summarized in Tables 6-8 of Section 16. Instrument conditions and columns should be optimized prior to the initiation of the IDC.

10.10.2 Establish an appropriate retention time window for each analyte. This should be based on measurements of actual retention time variation for each method analyte in CAL standard solutions analyzed on the LC over the course of time. A value of plus or minus three times the standard deviation of the retention time obtained for each method analyte while establishing the initial calibration and completing the IDC can be used to calculate a suggested window size. However, the experience of the analyst should weigh heavily on the determination of the appropriate retention window size.

10.10.3 Calibrate the system by either the analysis of a calibration curve (Sect. 10.6) or by confirming the initial calibration is still valid by analyzing a CCV as described in Section 10.7. If establishing an initial calibration, complete the IDC as described in Section 13.2.

10.10.4 Begin analyzing Field Samples, including QC samples, at their appropriate frequency by injecting the same size aliquots under the same conditions used to analyze the CAL standards.

10.10.5 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to identify peaks of interest in predetermined retention time windows. Use the data system software to examine the ion abundances of the peaks in the chromatogram. Identify an analyte by comparison of its retention time with that of the corresponding method analyte peak in a reference standard.

10.10.6 The analyst must not extrapolate beyond the established calibration range. If an analyte peak area exceeds the range of the initial calibration curve, the sample should be re-extracted with a reduced sample volume in order to bring the out of range target analytes into the calibration range. If a smaller sample size would not be representative of the entire sample, the following options are recommended. Re-extract an additional aliquot of sufficient size to insure that it is representative of the entire sample. Spike it with a higher concentration of internal standard. Prior to LC/MS analysis, dilute the sample so that it has a concentration of internal standard equivalent to that present in the calibration standard. Then, analyze the diluted extract.

11. Data Evaluation, Calculations and Reporting

11.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations using MS/MS. In validating this method, concentrations were calculated by measuring the product ions listed in Table 7.

11.2 Calculate analyte concentrations using the multipoint calibration established in Section 10.6. Do not use daily calibration verification data to quantitate analytes in samples. Adjust final analyte concentrations to reflect the actual sample volume determined in Section 10.6 where:

C_{ex} = (Area of target analyte * Concentration of Labeled analog) / (area of labeled analog * CF)

C_s = (C_{ex} / sample volume in ml) * 1000

C_{ex} = The concentration of the analyte in the extract
CF = calibration factor from calibration.

11.3 Prior to reporting the data, the chromatogram should be reviewed for any incorrect peak identification or poor integration.

11.4 PFHxS, PFOS, PFOA, NMeFOSAA, and NEtFOSAA have multiple chromatographic peaks using the LC conditions in Table 5 due to the linear and branch isomers of these compounds (Sect. 10.6.4.1). The areas of all the linear and branched isomer peaks observed in the CAL standards for each of these analytes must be summed and the concentrations reported as a total for each of these analytes.

11.5 Calculations must utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty), typically two, and not more than three significant figures.

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

12.1 Section 9.0 outlines sample batch QC acceptance criteria. If non-compliant organic compound results are to be reported, the Organic Section Head and/or the Laboratory Director, and the Operations Manager must approve the reporting of these results. The laboratory Project Manager shall be notified, and may choose to relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The analyst, Data Reviewer, or Department Supervisor performing the secondary review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

12.2 All results for the organic compounds of interest are reportable without qualification if extraction and analytical holding times are met, preservation requirements (including cooler temperatures) are met, all QC criteria are met, and matrix interference is not suspected during extraction or analysis of the samples. If any of the below QC parameters are not met, all associated samples must be evaluated for re-extraction and/or re-analysis.

13. Method Performance

13.1 Detection Limit Study (DL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

13.1.1 The laboratory follows the procedure to determine the DL, LOD, and/or LOQ as outlined in Alpha SOP ID 1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

13.2.1 The IDC must be successfully performed prior to analyzing any Field Samples. Prior to conducting the IDC, the analyst must first generate an acceptable Initial Calibration following the procedure outlined in Section 10.6.

13.2.2 INITIAL DEMONSTRATION OF LOW SYSTEM BACKGROUND – Any time a new lot of SPE cartridges, solvents, centrifuge tubes, disposable pipets, and autosampler vials are used, it must be demonstrated that an MB is reasonably free of contamination and that the criteria in Section 9.2.1 are met. If an automated extraction system is used, an MB should be extracted on each port to ensure that all the valves and tubing are free from potential PFAS contamination.

13.2.3 INITIAL DEMONSTRATION OF PRECISION (IDP) – Prepare, extract, and analyze four to seven replicate LCSs fortified near the midrange of the initial calibration curve according to the procedure described in Section 10. Sample preservatives as described in Section 6.2.1 must be added to these samples. The relative standard deviation (RSD) of the results of the replicate analyses must be less than 20%.

13.2.4 INITIAL DEMONSTRATION OF ACCURACY (IDA) – Using the same set of replicate data generated for Section 13.2.3, calculate average recovery. The average recovery of the replicate values must be within ± 30% of the true value.

13.2.5 INITIAL DEMONSTRATION OF PEAK ASYMMETRY FACTOR – Peak asymmetry factors must be calculated using the equation in Section 9.10.1 for the first two eluting peaks (if only two analytes are being analyzed, both must be evaluated) in a mid-level CAL standard. The peak asymmetry factors must fall in the range of 0.8 to 1.5. See guidance in Section 10.6.4.1 if the calculated peak asymmetry factors do not meet the criteria.

13.2.6 Refer to Alpha SOP ID 1739 for further information regarding IDC/DOC Generation.

13.2.7 The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

14.1 Refer to Alpha's Chemical Hygiene Plan and Hazardous Waste Management and Disposal SOP for further pollution prevention and waste management information.

14.2 This method utilizes SPE to extract analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby minimizing the potential hazards to both the analyst and the environment as compared to the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.3 The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents and solvents are used. The matrices of concern are finished drinking water or source water. However, laboratory waste management practices must be conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

15. Referenced Documents

Chemical Hygiene Plan – ID 2124

SOP ID 1732 Detection Limit (DL), Limit of Detection (LOD) & Limit of Quantitation (LOQ) SOP

SOP ID 1739 Demonstration of Capability (DOC) Generation SOP

SOP ID 1728 Hazardous Waste Management and Disposal SOP

16. Attachments

Table 7: LC Method Conditions

Time (min)	2 mM Ammonium Acetate (5:95 MeOH/H_2O)	100% Methanol
Initial	100.0	0.0
1.0	100.0	0.0
2.2	85.0	15.0
11	20.0	80.0
11.4	0.0	100.0
12.4	100.0	00.0
15.5	100.0	0.0
Waters Aquity UPLC ® BEHC_{18} 2.1 x 50 mm packed with 1.7 µm BEH C_{18} stationary phase Flow rate of 0.4 mL/min 2-5 µL injection		

Table 8: ESI-MS Method Conditions

ESI Conditions	
Polarity	Negative ion
Capillary needle voltage	.5 kV
Cone Gas Flow	25 L/hr
Nitrogen desolvation gas	1000 L/hr
Desolvation gas temp.	500 ºC

Table 9: Method Analyte Source, Retention Times (RTs), and EIS References

#	Analyte	Transition	RT	IS	Type
1	M3PBA	216>171	2.65		REC
2	PFBA	213 > 169	2.65	2: M4PFBA	
3	M4PFBA	217 > 172	2.65	1: M3PBA	EIS
4	PFPeA	263 > 219	5.67	4: M5PFPEA	
5	M5PFPEA	268 > 223	5.66	1: M3PBA	EIS
6	PFBS	299 > 80	6.35	6: M3PFBS	
7	M3PFBS	302 > 80	6.35	29:M4PFOS	EIS
8	FtS 4:2	327 > 307	7.47	9: M2-4:2FTS	

#	Analyte	Transition	RT	IS	Type
9	M2-4:2FTS	329 > 81	7.47	29:M4PFOS	EIS
10	PFHxA	303 > 269	7.57	10: M5PFHxA	
11	M5PFHxA	318 > 273	7.57	19:M2PFOA	EIS
12	PFPeS	349 > 80	7.88	18: M3PFHxS	
13	PFHpA	363 > 319	8.80	14: M4PFHpA	
14	M4PFHpA	367 > 322	8.80	19:M2PFOA	EIS
15	L-PFHxS	399 > 80	8.94	18: M3PFHxS	
16	br-PFHxS	399 > 80	8.72	18: M3PFHxS	
17	PFHxS Total	399 > 80	8.94	18: M3PFHxS	
18	M3PFHxS	402 > 80	8.94	29:M4PFOS	EIS
19	MPFOA	415 > 370	9.7		REC
20	PFOA	413 > 369	9.7	23: M8PFOA	
21	br-PFOA	413 > 369	9.48	23: M8PFOA	
22	PFOA Total	413 > 369	9.7	23: M8PFOA	
23	M8PFOA	421 > 376	9.7	19: M2PFOA	EIS
24	FtS 6:2	427 > 407	9.66	25: M2-6:2FTS	
25	M2-6:2FTS	429 > 409	9.66	29:M4PFOS	EIS
26	PFHpS	449 > 80	9.78	33: M8PFOS	
27	PFNA	463 > 419	10.41	33: M8PFOS	
28	M9PFNA	472 > 427	10.41	19: M2PFOA	EIS
29	M4PFOS	501 > 80	10.45		REC
30	PFOS	499 > 80	10.45	33: M8PFOS	
31	br-PFOS	499 > 80	10.27	33: M8PFOS	
32	PFOS Total	499 > 80	10.45	33: M8PFOS	
33	M8PFOS	507 > 80	10.45	29: M4PFOS	EIS
34	FtS 8:2	527 > 507	10.99	38: M2-8:2FTS	
35	M2-8:2FTS	529 > 509	10.99	29:M4PFOS	EIS
36	M2PFDA	515 > 470	11.00		REC
37	PFDA	513 > 469	11.00	38: M6PFDA	
38	M6PFDA	519 > 474	11.00	36: M2PFDA	EIS
39	PFNS	549 > 80	11.02	33:M8PFOS	
40	NMeFOSAA	570 > 419	11.41	41: D3-NMeFOSAA	
41	d3-NMeFOSAA	573 > 419	11.41	36: M2PFDA	EIS
42	PFOSA	498 > 78	11.48	29: M8FOSA	
43	M8FOSA	506 > 78	11.48	19: M2PFOA	EIS
44	PFUnDA	563 > 519	11.51	41: M7-PFUDA	
45	M7-PFUDA	570 > 525	11.51	36: M2PFDA	EIS
46	PFDS	599 > 80	11.51	33:M8PFOS	
47	NEtFOSAA	584 > 419	11.68	48: d5-NEtFOSAA	

#	Analyte	Transition	RT	IS	Type
48	d5-NEtFOSAA	589 > 419	11.68	36: M2PFDA	EIS
49	PFDoA	613 > 569	11.96	50: MPFDOA	
50	MPFDOA	615 > 570	11.96	36: M2PFDA	EIS
51	PFTriA	663 > 619	12.34	50: MPFDOA	
52	PFTeA	713 > 669	12.6	53: M2PFTEDA	
53	M2PFTEDA	715 > 670	12.6	36: M2PFDA	EIS
54	M3HFPO-DA	329>285	7.97	19: M2PFOA	EIS
55	HFPO-DA	332>287	7.97	54: M3HFPO-DA	
56	ADONA	377>251	8.00	23: M8PFOA	
57	PFHxDA	813>769	13.20	59: M2PFHxDA	
58	PFODA	913>869	13.50	59: M2PFHxDA	
59	M2PFHxDA	815>770	13.20	36:M2PFDA	EIS
60	NEtFOSA	526>169	11.00	61: NMeFOSA	
61	NMeFOSA	512>169	10.50	63: d3-NMeFOSA	
62	d3-NMeFOSA	515>169	10.50	29: M4PFOS	EIS
63	d5-NEtFOSA	531>169	11.00	29: M4PFOS	EIS
64	NMeFOSE	556>122	11.25	66: d7-NMeFOSE	
65	NEtFOSE	570>136	10.75	67: d9-NEtFOSE	
66	d7-NMeFOSE	563>126	11.25	29: M4PFOS	EIS
67	d9-NEtFOSE	579>142	10.75	29: M4PFOS	EIS
68	FtS 10:2	627>607	11.50	25: M2-6:2FTS	
69	PFDoS	699>99	12.50	33: M8PFOS	

Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)

Reference Method No.: **EPA 8270 D**

Reference: SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update V, February 2007.

1. Scope and Application

Matrices: This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, and wastewater samples.

This method is used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone.

Table 9 lists “difficult” compounds that may require special treatment when being determined by this method.

Approval of any method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability (Section 13.2).

2. Summary of Method

The samples are introduced into the GC/MS by injecting 1µL of the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

Analytes eluted from the capillary column are introduced into the mass spectrometer via direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of standards run on the same GC/MS system. Quantitation is accomplished by comparing the response of quantitation ion relative to an internal standard using a calibration curve.

2.1 Method Modifications from Reference

None.

3. Reporting Limits

Table 6 lists our routine reporting limits.

4. Interferences

4.1 Only high purity helium is used in the GC system to eliminate this source of possible contamination. The helium (carrier gas) is certified by the gas supplier.

4.2 Preventive instrument maintenance is performed routinely. Section 10.5 details the maintenance steps.

4.3 Glassware must be scrupulously cleaned. This procedure is detailed in the Organic Extraction Glassware Cleaning & Handling SOP/1953.

4.4 Contaminated solvents or reagents are also possible sources of contamination. All solvents used are pesticide grade or equivalent, and reagents are purchased as certified contaminant free.

4.5 Contamination by carry-over can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered (concentrations greater than 2x the highest concentration) and the next sample has reportable hits this sample should to be re-analyzed for confirmation based on analyst discretion.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.1 Lab coats, safety glasses, and gloves must be worn when handling samples, extracts, standards or solvents.

5.2 All solvent and extract transfers must be handled in the vented bench area in the GC/MS laboratory.

5.3 All stock standards, working standards, and vialed sample extracts must be placed into the waste bucket in the lab for future disposal by the Health and Safety Officer. The container must be labeled properly with hazard warning labels indicating the container contents.

5.4 Flammable solvent bottles must be stored in the flammables cabinet.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Aqueous samples are collected in two 1L amber glass jars with teflon-lined lids. For LVI, aqueous samples are collected in two 275mL amber glass jars with teflon-lined lids. Solid samples are collected in 250mL wide-mouth glass jars with teflon-lined lids. All containers are purchased pre-cleaned and certified from commercial vendors.

6.2 Sample Preservation

Both aqueous and solid samples are then preserved by packing in coolers with ice or ice packs, to maintain a temperature of 4 ± 2ºC. Upon receipt at the laboratory, the samples are transferred into sample storage refrigerators to maintain at a temperature of 4 ± 2ºC.

6.3 Sample Handling

Aqueous samples must be extracted within 7 days of sample collection, solid samples within 14 days of collection. Once extracted, the samples must be analyzed within 40 days of the extraction date.

7. Equipment and Supplies

7.1 Gas Chromatograph/Mass Spectrometer System:

7.1.1 Gas Chromatograph, Hewlett Packard 6890 (or equivalent): An analytical system complete with a temperature-programmable gas chromatograph configured for split/splitless-injection and all required accessories, including syringes, analytical columns, and gases. The capillary column is directly coupled to the source.

7.1.2 Column: Rxi-5Sil MS30m x 0.32mm ID, 0.25µm film thickness or column of similar configuration.

7.1.3 Mass Spectrometer, Hewlett Packard 5973 (or equivalent): Scanning from 35 to 500 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer is capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 1 when 1 µL of the GC/MS tuning standard is injected through the GC (50ng of DFTPP).

7.1.4 Data System: A computer system is interfaced to the Mass Spectrometer. The system allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer software allows the analyst to search for any GC/MS data file for ions of specific mass and plot such ion abundances versus time or scan number. *HP ChemServer* software is used for data acquisition and *MSD Chemstation/Enviroquant version E.02.02* is used for data reduction.

7.2 Syringe: 10 µL.

7.3 Volumetric Flasks, Class A: Appropriate sizes with ground-glass stoppers.

7.4 Vials: Glass autosampler vials with polytetrafluoroethylene (PTFE)-lined crimp top caps.

8. Reagents and Standards

8.1 Stock Standard Solutions

Certified stock standard solutions, traceable to NIST, when available, are purchased from commercial vendors. They can be replaced with different standards as long as they contain all target analytes.

All stock standards, lot number, catalog number, expiration date, preparation date and initials are recorded in a logbook. Standards are stored in the refrigerator or freezer.

Stock standard expire 6 months from the date of preparation or on the earliest expiration date of any of the stock solution used to prepare it.

Please note that the following preparation instructions and stock standards are included for illustration purposes and may be modified as needed (ex. to accommodate standard availability or client requests), however final concentrations for the initial calibration levels shall always follow the example in 8.1.4.

Vendor	Standard	Catalog#	Concentration
Restek			
	8270 Mega Mix	31850	500-1000ug/mL
	Benzoic Acid Mix	31879	2000ug/mL
	Acid Surrogate Mix	31087	10000ug/mL
	B/N Surrogate Mix	31086	5000ug/mL
	Benzaldehyde Standard	33017	2000ug/mL
	Custom AP9 ICAL Standard	571813-FL	2000ug/mL
	Custom ADP Standard	572745-FL	2000ug/mL
	Benzidine Mix	31834	2000ug/mL
	SV Internal Standard Mix	31206	2000ug/mL
	1,4-Dioxane	30287	2000ug/mL
	Custom CLP 04.1 BNA Surrogate Mix	571320-FL	1000ug/mL
Absolute			
	Aromatic Amines Mix	99410	2000ug/ml
Ultra			
	Semi-Volatiles GC/MS Tuning Standard	GCM-150-1	1000ug/mL

8.1.1 ABN Stock Standard, 200ug/mL

Use 5mL of each of the following:
- Benzoic Acid Mix
- Benzidine Mix

and use 10mL of each of the following:
- 8270 Mega Mix
- Custom CLP 04.1 BNA Surrogate Mix

Bring up to 50mL volume with DCM.

8.1.2 AP9 Additional Compounds Stock Standard, 200ug/mL

Use 5mL of each of the following:
- Custom AP9 ICAL Standard
- Benzaldehyde Standard

Bring up to 50mL volume with DCM.

8.1.3 ADP Stock Standard, 200ug/ml

Use 5ml of:
Custom ADP Standard

Bring up to 50mL volume with DCM.

8.1.4 Calibration Standard

A minimum of 5 calibration standards must be included for each analyte:

Calibration Curve Levels	
Level	Concentration ug/mL
1	1.0
2	2.0
3	3.0
4	5.0
5	10
6	20
7	50
8	100
9	150
10	200

LVI Calibration Curve Levels	
Level	Concentration ug/mL
1	0.2
2	0.4
3	1.0
4	2.0
5	3.0
6	5.0
7	10
8	15
9	35
10	50

*LVI- Low Volume Initiative

8.2 Internal Standard Solution

The internal standards are:
1,4-dichlorobenzene-d_4
naphthalene-d_8
acenaphthene-d_{10}
phenanthrene-d_{10}
chrysene-d_{12}
perylene-d_{12}

Each 500µL of standards, blank and sample extracts are spiked with 10µL of SV Internal Standard Mix, resulting in a concentration of 40ng/ µL.

For the LVI method, a 1:10 dilution is made of the Internal Standard Stock Solution. 500µL of standards, blank and sample extracts are spiked with 10µL of this preparation, resulting in a concentration of 4ng/ µL.

8.3 GC/MS Tuning Standard

The tuning standard is a methylene chloride solution containing 50ng/µL of decafluorotriphenylphosphine (DFTPP). The standard also contains 50ng/µL each of 4,4'DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance.

Prepare the GC/MS Tuning Standard with 25µL GCM-150 and 475µL Dichloromethane.

8.4 Surrogate Spiking Solution

8.4.1 Extraction Surrogate Preparation

In a 1000mL volumetric flask, add 5ml of 31086 and 31087. Bring up to volume with Acetone. The final concentration is 50µg/mL for the acid surrogates and 25µg/mL for the B/N surrogates.

8.4.2 LVI Extraction Surrogate Preparation

The LVI surrogate is a 10 fold dilution of the surrogate solution prepared in 8.4.1. For example, to make 200mL of LVI surrogate, add 20mL of 8.4.1 to a 200mL volumetric flask and fill to volume with Acetone. The resulting surrogate concentration is 5µg/mL for the acid surrogates and 2.5µg/mL for the B/N surrogates.

8.5 Spike Solution (LCS, MS, MSD)

Spike Solution Preparation

ABN SPK1:
In a 500ml volumetric flask, add 20ml of 8270 Mega Mix #31850, 10ml of Benzoic Acid Mix #31879, 10ml Custom AP9 ICAL Standard #571813-FL and 10ml Benzaldehyde Standard #33017. Bring up to volume with Acetone. The final concentration is 40µg/ml.

Note: the LVI ABN SPK1 is prepared by making an 8 fold dilution of the 40µg/ml ABN SPK (in acetone), resulting in a 5µg/ml LVI ABN SPK1.

ABN SPK2:
In a 500ml volumetric flask, add 10ml Benzidine Mix #31834 and 10mL Custom ADP Standard #572945-FL. Bring up to volume with Acetone. The final concentration is 40µg/ml.

Note: the LVI ABN SPK2 is prepared by making an 8 fold dilution of the 40µg/ml ABN SPK (in acetone), resulting in a 5µg/ml LVI ABN SPK2.

8.6 Dichloromethane (DCM): Pesticide quality.

8.7 Acetone: Pesticide quality.

9. Quality Control

9.1 Blank(s)

Extraction blanks are performed with each extraction batch of 20 or less samples. The extraction blank must not contain any of the reportable analytes above the reporting limit. Corrective actions:

- No corrective action required if concentration of contaminant in sample is >10x concentration in blank or if contaminant not detected in sample

- If the blank have reportable hits and re-extraction could not be performed due to lack of additional sample volume, the sample results are reported and qualified with “B” flag for any associated samples that concentration is less than 10x the blank concentration

For NJ regulatory work the method blank must have all the target analytes less than RL except for Phthalates which must be less than 5x of the RL. Sample results are qualified with

"B" flag for analytes observed in the blank greater than RL and the Phthalates observed in the blank greater than 5x RL

The surrogate recoveries must also be within the acceptance criteria listed in Table 2. If surrogate acceptance criteria are exceeded, the extraction batch must be evaluated to determine if re-extraction or re-analysis is necessary.

9.2 Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS / LCSD)

A Laboratory Control Sample/Laboratory Control Sample Duplicate pair (LCS/LCSD) are extracted and analyzed with each analytical batch of 20 or fewer samples.

The LCS/LCSD acceptance criteria are based on in-house control limits. Less than 10% of total compounds may be outside of control limits provided that recoveries are >10%. Note: this does not apply to difficult analytes listed in Table 9 which may be accepted at recoveries <10. If >10% of analytes are recovered above control limits, this is deemed acceptable as long as the analytes in question are not detected in associated samples.

If these criteria are not met, the entire batch is re-extracted. If re-extraction is not possible, due to insufficient sample or holding time exceedance, the analyst must write up the failure on a narrative sheet for inclusion in the client report.

9.3 Initial Calibration Verification (ICV)

Refer to Section 10.2.7.

9.4 Continuing Calibration Verification (CCV)

Refer to Section 10.4.

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

A matrix spike/matrix spike duplicate pair is extracted and analyzed for each batch of 20 or fewer samples per client request. The MS/MSD acceptance criteria are based on in-house control limits. If the recovery criteria are not met, but are met in the LCS/LCSD, this is noted on a narrative sheet for inclusion in the client report.

9.6 Laboratory Duplicate

Not applicable.

9.7 Method-specific Quality Control Samples

9.7.1 Surrogates

All extracted samples and associated QC are spiked with surrogates. The acceptable surrogate recovery limits are listed in Table 2.

Corrective action: Up to one surrogate can be out in each fraction (Acid and Base/Neutral) but not less than 10% recovery, before any corrective action is necessary. Otherwise, analysis must be repeated once to see if an analytical error has occurred. If the % recovery still exceeds the control limits the sample must be re-extracted and re-analyzed to confirm sample matrix. If matrix effect is confirmed, this must be noted on a narrative sheet for inclusion in the client report.

Re-extraction is not required if surrogate recoveries are high and target analytes are not detected in the sample.

9.7.2 Internal Standards

If the area for any of the internal standards in the samples changes by a factor of two (-50% to +100%) from that in the CCV, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

9.8 Method Sequence

In a 12-hour period, the typical analytical sequence is:

- Degradation Check
- DFTPP
- Continuing or Daily Standards (1 – 3)*
  (1) ABN 50 ppm
  (2) AP9 50 ppm
  (3) ADP 50 ppm
- Method Blank
- Samples
- QC (as required)

***Additional Continuing standards may be run at the analyst's discretion or by client request.**

10. Procedure

10.1 Equipment Set-up

10.1.1 GC/MS Operating Conditions:

Typical GC/MS operating conditions are listed below, but may be altered as long as method performance criteria are met.

Mass range:	35 – 500 amu
Scan time:	3.15 second / scan
Initial temperature:	50°C, hold for 1.5 minutes
Temperature program:	28°C/minute to 250°C then 9°C/minute to 320°C
Final temperature:	320°C for 1.50 min
Injector temperature:	300°C
Transfer line temperature:	280°C
Source temperature:	230ºC
Injector:	split ratio 5:1; 11.7mL/min
Injection volume:	1µL
Carrier gas:	helium at 523 cm/second (2.0 mL/min) constant flow

GC/MS Operating Conditions for LVI method:

Mass range:	35 – 550 amu
Scan time:	3.15 second / scan
Initial temperature:	45°C, hold for 4 minutes
Temperature program:	25°C/minute to 250°C then 20°C/minute to 320°C
Final temperature:	320°C for 4.3 min
Injector temperature:	270°C
Transfer line temperature:	280°C
Source temperature:	320ºC
Injector:	split ratio 5:1; 8.57mL/min

Injection volume:	2µL
Carrier gas:	helium at 1.7148mL/min) constant flow

10.1.2 GC/MS Tune:

At the beginning of every 12 hour sequence, analyze DFTPP tuning solution (Section 8.3).

The resultant mass spectrum for DFTPP must meet the criteria given in Table 1 before sample analysis begins. The mass spectrum of DFTPP should be acquired in the following manner:

(1) Three scans (the peak apex scan, the scan immediately preceding the apex and the scan immediately following the apex) are acquired and averaged.
(2) Background subtraction is performed using a single scan of no more than 20 scans prior to the elution of DFTPP.

The GC/MS tuning standard is also used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD must not exceed 20%. Benzidine and pentachlorophenol must be present at their normal responses and no peak tailing must be visible.

The tailing factor for benzidine and pentachlorophenol must be calculated in every DFTPP run. (See Table 4)

If degradation is excessive and/or poor chromatography is noted, the system needs maintenance (see Section 10.5).

10.2 Initial Calibration

10.2.1 Prepare calibration standards for all target analytes at a minimum of five concentration levels as specified in Section 8.1.4.

10.2.2 Add 10µL of Internal Standard to each calibration standard directly into the autosampler vial containing 500µL of standard. Analyze each calibration standard under the conditions specified in Section 10.1.1.

10.2.3 Record the calibration standard, unique lab identifier code (lot), concentration, and analyst's initials in the analytical sequence list.

10.2.4 In each standard, calculate the response factor (RF) for each analyte, the average RF, and the relative standard deviation (RSD) of the RFs, using the Enviroquant data processing software. The calculations are performed automatically, using the formulae listed in Alpha's Quality Manual.

It is recommended that a minimum response factor for the most common target analytes, as noted in Table 8, be demonstrated for each individual calibration level as a means to ensure that these compounds are behaving as expected. In addition, meeting the minimum response factor criteria for the lowest calibration standard is critical in establishing and demonstrating the desired sensitivity.

10.2.5 Initial Calibration %RSD Criteria:

For all analytes, the RSD must be ≤ 20% for the mean response factor to be used for sample quantitation.

For RCP, the RSD must be ≤ 15% for the mean response factor to be used for sample quantitation.

An alternate calculation fits may be performed provided that the minimum correlation coefficient ≥ 0.99 is met.

When linear regression model is used a minimum quantitation check of the lowest calibration point is performed. The recalculated concentration of the low calibration point should be within ± 30% of the standard's true concentration.

10.2.6 Evaluation of Retention Times:

The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units.

10.2.7 Initial Calibration Verification (Second Source Verification)

10.2.7.1 The initial calibration (Section 10.2) for each compound of interest must be verified prior to sample analysis. This is accomplished by analyzing second source calibration standards at a concentration near the midpoint concentration for the calibrating range of the GC/MS.

10.2.7.2 Analyze the standards and calculate the % Difference for each analyte according to the formula in Alpha's Quality Manual.

If the % Difference for each analyte is ± 30%, then the calibration is assumed to be valid. If this criterion is not met, then corrective action must be taken prior to the analysis.

For RCP, if the % Difference for each analyte is ± 20%, then the calibration is assumed to be valid. If this criterion is not met, then corrective action must be taken prior to the analysis.

10.2.7.3 In cases where compounds fail (greater than 30% difference), they may still be reported as non-detects.

10.3 Equipment Operation and Sample Processing

GC/MS Analysis of Samples

10.3.1.1 Allow the sample extracts to warm to room temperature.

10.3.1.2 Transfer all of the sample extract to a 1.5mL vial. Remove 500µL of sample extract to another vial, and add 10µL of the internal standard solution (Section 8.2).

10.3.1.3 The autosampler is programmed to inject 1µL aliquot of the sample extract into the GC/MS system, using the same instrument conditions that were used for calibration. The injection volume of the sample must be the same as the volume used for the calibration standard.

10.3.1.4 If the response of any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed.

10.3.2 Qualitative Identification

Perform first level data review. Obtain the primary m/z (Table 5) masses for each parameter of interest. The following criteria must be met to make qualitative identification:

- Compare the background subtracted mass spectra for the sample to the reference spectra. The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.
- The retention time must fall within ± 0.1 minutes of the retention time of the compound in the analytical standard. However, analyst experience must be used in making the qualitative identification.
- The relative peak height of the one characteristic mass must fall within 30% of the relative intensity of the mass in a reference mass spectrum. The reference spectrum is obtained from a standard analyzed on the GC/MS system.

Structural isomers that have very similar mass spectra are identified only if the resolution between authentic isomers in a standard mix is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

10.4 Continuing Calibration

10.4.1 The initial calibration (Section 10.2) for each compound of interest must be verified once every 12 hours prior to sample analysis. This is accomplished by analyzing calibration standards at a concentration near the midpoint concentration for the calibrating range of the GC/MS.

10.4.2 Analyze the standards and calculate the % Difference for each analyte according to the formula in Alpha's Quality Manual.

If the % Difference for each CCV analyte is $\leq$ 20%, then the calibration is assumed to be valid. If the criterion is not met for more than 20% of the compounds then corrective action must be taken.

Due to the large number of analytes present, allowances may be made for a RF that drifts out high, as long as there are no positive hits for that particular analyte in any of the associated samples.

10.4.3 If this criterion is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

10.4.4 If routine maintenance does not return the instrument performance to meet the QC requirements based on the last initial calibration, then a new initial calibration must be performed.

10.4.5 Internal Standard Retention Time

The retention times of the internal standards in the calibration verification standard is evaluated after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard of the most recent initial calibration, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

10.4.6 Internal Standard Response

Refer to section 9.7.2

10.5 Preventive Maintenance

When poor sensitivity is observed, replacement of the injector liner and seal may solve the problem. If not, clip approximately 3 – 6 inches from the injector end of the GC column. If the sensitivity does not improve it may be necessary to replace the split line or the injector weldment assembly. If the problem persists, it may be necessary to replace the GC column.

Periodic cleaning (typically twice per year) of the mass spectrometer ion source is required. More frequent source cleaning may be needed, especially if dirty samples are analyzed.

11. Data Evaluation, Calculations and Reporting

When a parameter is identified, the quantitation of that parameter must be based on the integrated abundance of the quantitation characteristic m/z given in Table 5

Calculate the concentration in the sample using the average response factor (RF) from the initial calibration curve according to the formula in Alpha's Quality Manual.

After performing technical data review, validating that all QC criteria have been met and confirming all positive hits, the data report is sent electronically to the LIMS computer for generation of the client report. There are two levels of review of the data in the LIMS system prior to release of data. These reviews must be done by two separate individuals.

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

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Perform instrument maintenance as described throughout this SOP as needed when instrument calibration criteria are not met. Record all maintenance in the instrument logbook.

All batch and sample specific QC criteria outlined in Section 9 are evaluated by the analyst prior to approval of the data. When any QC criteria fail, the cause for the failure must be identified and corrected. This may include instrument recalibration followed by sample reanalysis, sample cleanup, or sample re-extraction. If it is determined that the failure is due to sample matrix effects, a project narrative report is written by the analyst for inclusion in the data report. If there is insufficient sample volume to perform the re-analysis for confirmation, this is also noted in the narrative and included in the client report.

13. Method Performance

13.1 Detection Limit Study (DL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the DL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

Alpha SOP/1732 DL/LOD/LOQ Generation

Alpha SOP/1739 IDC/DOC Generation

Alpha SOP/1729 Waste Management and Disposal SOP

16. Attachments

Table 1: DFTPP Key Ions and Ion Abundance Criteria

Table 2: Acceptable Surrogate Spike Recovery Limits

Table 3A: Acceptable Aqueous QC Limits

Table 3B: Acceptable Soil QC Limits

Table 4: Tailing Factor Calculation

Table 5: Characteristic Ions for Semivolatile Compounds

Table 6: Reported Detection Limits

Table 7: Semivolatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

Table 8: Recommended Minimum Response Factor Criteria

Table 9: Difficult analytes

TABLE 1

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	10-80% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	10-80% of mass 198
197	< 2% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-60% of mass 198
365	> 1% of mass 198
441	Present but less than 24% mass 442
442	> 50% of mass 198
443	15-24% of mass 442

TABLE 2

ACCEPTABLE SURROGATE SPIKE RECOVERY LIMITS

Analytical Fraction	Surrogate Compound	Water	Soil/Sediment
BN-8270D	Nitrobenzene-d_5	23-120%	23-120%
BN-8270D	2-Fluorobiphenyl	15-120%	30-120%
BN-8270D	p-Terphenyl-d_{14}	41-149%	18-120%
Acid-8270D	Phenol-d_6	10-120%	10-120%
Acid-8270D	2-Fluorophenol	21-120%	25-120%
Acid-8270D	2,4,6-Tribromophenol	10-120%	10-136%

It is allowable for one surrogate from each fraction be outside acceptance criteria, provided a minimum recovery of 10% has been achieved.

TABLE 3A

ACCEPTABLE AQUEOUS QC LIMITS

	STANDARD TARGET COMPOUND LIST (Aqueous)		NEW JERSEY TARGET COMPOUND LIST (Aqueous)		CT TARGET COMPOUND LIST (Aqueous)	
Analyte	**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**
1,2,4,5-Tetrachlorobenzene			70-130	20	40-140	20
1,2,4-Trichlorobenzene	39-98	30	70-130	20	40-140	20
1,2-Dichlorobenzene	40-140	30	70-130	20		
1,3-Dichlorobenzene	40-140	30	70-130	20		
1,3-Dinitrobenzene	15-130	30				
1,4-Dichlorobenzene	36-97	30	70-130	20		
1-Methylnaphthalene	41-103	30				
2,3,4,6-Tetrachlorophenol			70-130	20		
2,4,5-Trichlorophenol	30-130	30	70-130	20	30-130	20
2,4,6-Trichlorophenol	30-130	30	70-130	20	30-130	20
2,4-Dichlorophenol	30-130	30	70-130	20	30-130	20
2,4-Dimethylphenol	30-130	30	70-130	20	30-130	20
2,4- Dimethylaniline	40-140	30	70-130	20		
3,4- Dimethylaniline	40-140	30	70-130	20		
2,3- Dimethylaniline	40-140	30	70-130	20		
2,4,5-Dimethylaniline	40-140	30	70-130	20		
4-Chlorotoluidine	40-140	30	70-130	20		
2-Ethylaniline	40-140	30	70-130	20		
O-toluidine	40-140	30	70-130	20		
2-Napthylamine	40-140	30	70-130	20		
2,4-Dinitrophenol	20-130	30	20-130	20	30-130	20
2,4-Dinitrotoluene	24-96	30	70-130	20	40-140	20
2,6-Dinitrotoluene	40-140	30	70-130	20	40-140	20
2-Chloronaphthalene	40-140	30	70-130	20	40-140	20
2-Chlorophenol	27-123	30	70-130	20	30-130	20
2-Methylnaphthalene	40-140	30	70-130	20	40-140	20
2-Methylphenol	30-130	30	70-130	20	30-130	20
2-Nitroaniline	52-143	30	70-130	20	40-140	20
2-Nitrophenol	30-130	30	70-130	20	30-130	20
3,3'-Dichlorobenzidine	40-140	30	70-130	20	40-140	20
3,3'-Dimethylbenzidine			20-160	20		
3-Methylphenol/4-Methylphenol	30-130	30	20-160	20	30-130	20
3-Nitroaniline	25-145	30	70-130	20	40-140	20
4,6-Dinitro-o-cresol	20-164	30	70-130	20	30-130	20
4-Bromophenyl phenyl ether	40-140	30	70-130	20	40-140	20
4-Chloroaniline	40-140	30	20-160	20	40-140	20
4-Chlorophenyl phenyl ether	40-140	30	70-130	20	40-140	20
4-Nitroaniline	51-143	30	70-130	20	40-140	20
4-Nitrophenol	10-80	30	20-160	20	30-130	20
Acenaphthene	37-111	30	70-130	20	40-140	20
Acenaphthylene	45-123	30	70-130	20	40-140	20

	STANDARD TARGET COMPOUND LIST (Aqueous)		NEW JERSEY TARGET COMPOUND LIST (Aqueous)		CT TARGET COMPOUND LIST (Aqueous)	
Analyte	**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**
Acetophenone	39-129	30	70-130	20		
Aniline	40-140	30	20-160	20	40-140	20
Anthracene	40-140	30	70-130	20	40-140	20
Atrazine			70-130	20		
Azobenzene	40-140	30	70-130	20		
Benzaldehyde			20-160	20		
Benzidine	10-75	30	20-160	20		
Benzo(a)anthracene	40-140	30	70-130	20	40-140	20
Benzo(a)pyrene	40-140	30	70-130	20	40-140	20
Benzo(b)fluoranthene	40-140	30	70-130	20	40-140	20
Benzo(ghi)perylene	40-140	30	70-130	20	40-140	20
Benzo(k)fluoranthene	40-140	30	70-130	20	40-140	20
Benzoic Acid	10-164	30	20-160	20		
Benzyl Alcohol	26-116	30	20-160	20		
Biphenyl	40-140	30	70-130	20		
Bis(2-chloroethoxy)methane	40-140	30	70-130	20	40-140	20
Bis(2-chloroethyl)ether	40-140	30	70-130	20	40-140	20
Bis(2-chloroisopropyl)ether	40-140	30	70-130	20	40-140	20
Bis(2-Ethylhexyl)phthalate	40-140	30	70-130	20	40-140	20
Butyl benzyl phthalate	40-140	30	70-130	20	40-140	20
Caprolactam			20-160	20		
Carbazole	55-144	30	70-130	20	40-140	20
Chrysene	40-140	30	70-130	20	40-140	20
Dibenzo(a,h)anthracene	40-140	30	70-130	20	40-140	20
Dibenzofuran	40-140	30	70-130	20	40-140	20
Diethyl phthalate	40-140	30	70-130	20	40-140	20
Dimethyl phthalate	40-140	30	70-130	20	40-140	20
Di-n-butylphthalate	40-140	30	70-130	20	40-140	20
Di-n-octylphthalate	40-140	30	70-130	20	40-140	20
Fluoranthene	40-140	30	70-130	20	40-140	20
Fluorene	40-140	30	70-130	20	40-140	20
Hexachlorobenzene	40-140	30	70-130	20	40-140	20
Hexachlorobutadiene	40-140	30	70-130	20	40-140	20
Hexachlorocyclopentadiene	40-140	30	20-160	20	40-140	20
Hexachloroethane	40-140	30	20-160	20	40-140	20
Indeno(1,2,3-cd)Pyrene	40-140	30	70-130	20	40-140	20
Isophorone	40-140	30	70-130	20	40-140	20
Naphthalene	40-140	30	70-130	20	40-140	20
Nitrobenzene	40-140	30	70-130	20	40-140	20
NitrosoDiPhenylAmine(NDPA)/ Diphenylamine (DPA)	40-140	30	70-130	20	40-140	20
n-Nitrosodimethylamine	22-74	30	20-160	20		
n-Nitrosodi-n-propylamine	29-132	30	70-130	20	40-140	20
P-Chloro-M-Cresol	23-97	30	70-130	20	30-130	20
Pentachlorophenol	9-103	30	20-160	20	30-130	20
Pentachloronitrobenzene					40-140	20

	STANDARD TARGET COMPOUND LIST (Aqueous)			NEW JERSEY TARGET COMPOUND LIST (Aqueous)		CT TARGET COMPOUND LIST (Aqueous)	
Analyte	**Acceptance Criteria**	**Duplicate RPD**		**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**
Phenanthrene	40-140	30		70-130	20	40-140	20
Phenol	12-110	30		20-160	20	30-130	20
Pyrene	26-127	30		70-130	20	40-140	20
Pyridine	10-66	30				40-140	20
2-Fluorophenol	*21-120*			*15-110*		*15-110*	
Phenol-d6	*10-120*			*15-110*		*15-110*	
Nitrobenzene-d5	*23-120*			*30-130*		*30-130*	
2-Fluorobiphenyl	*15-120*			*30-130*		*30-130*	
2,4,6-Tribromophenol	*10-120*			*15-110*		*15-110*	
4-Terphenyl-d14	*41-149*			*30-130*		*30-130*	

TABLE 3B

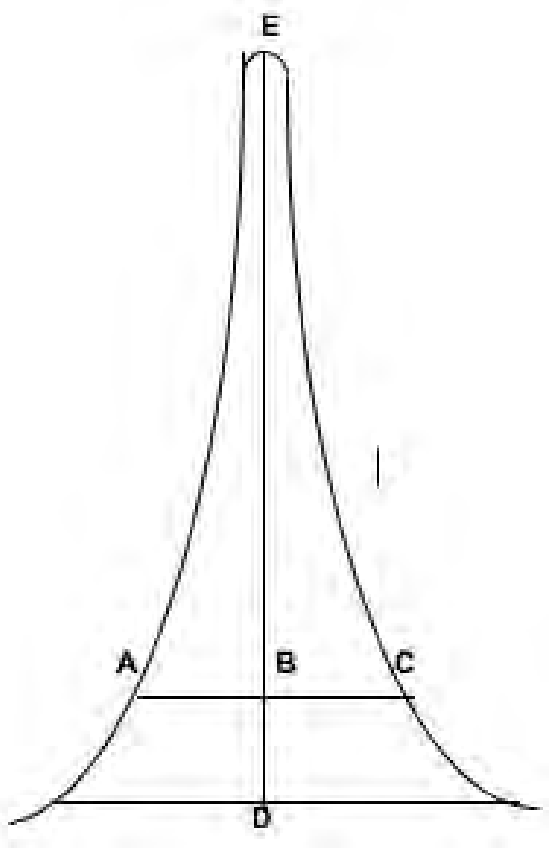
ACCEPTABLE SOIL QC LIMITS

	STANDARD TARGET COMPOUND LIST (Soil)		NEW JERSEY TARGET COMPOUND LIST (Soil)		CT TARGET COMPOUND LIST (Soil)	
Analyte	**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**
1,2,4,5-Tetrachlorobenzene	40-117	50	70-130	30	40-140	30
1,2,4-Trichlorobenzene	38-107	50	70-130	30	40-140	30
1,2-Dichlorobenzene	40-140	50	70-130	30		
1,3-Dichlorobenzene	40-140	50	70-130	30		
1,3-Dinitrobenzene	40-140	50				
1,4-Dichlorobenzene	28-104	50	70-130	30		
1-Methylnaphthalene	26-130	50				
2,3,4,6-Tetrachlorophenol	40-140	50	70-130	30		
2,4,5-Trichlorophenol	30-130	50	70-130	30	30-130	30
2,4,6-Trichlorophenol	30-130	50	70-130	30	30-130	30
2,4-Dichlorophenol	30-130	50	70-130	30	30-130	30
2,4-Dimethylphenol	30-130	50	70-130	30	30-130	30
2,4-Dinitrophenol	4-130	50	20-160	30	30-130	30
2,4-Dinitrotoluene	28-89	50	70-130	30	40-140	30
2,6-Dinitrotoluene	40-140	50	70-130	30	40-140	30
2-Chloroaniline	30-130	50				
2-Chloronaphthalene	40-140	50	70-130	30	40-140	30
2-Chlorophenol	25-102	50	70-130	30	30-130	30
2-Methylnaphthalene	40-140	50	70-130	30	40-140	30
2-Methylphenol	30-130.	50	70-130	30	30-130	30
2-Nitroaniline	47-134	50	70-130	30	40-140	30
2-Nitrophenol	30-130	50	70-130	30	30-130	30
3,3'-Dichlorobenzidine	40-140	50	70-130	30	40-140	30
3,3'-Dimethylbenzidine	15-115	50				
3-Methylphenol/4-Methylphenol	30-130	50	20-160	30	30-130	30
3-Nitroaniline	26-129	50	70-130	30	40-140	30
4,6-Dinitro-o-cresol	10-130	50	70-130	30	30-130	30
4-Bromophenyl phenyl ether	40-140	50	70-130	30	40-140	30
4-Chloroaniline	40-140	50	20-160	30	40-140	30
4-Chlorophenyl phenyl ether	40-140	50	70-130	30	40-140	30
4-Nitroaniline	41-125	50	70-130	30	40-140	30
4-Nitrophenol	11-114	50	20-160	30	30-130	30
Acenaphthene	31-137	50	70-130	30	40-140	30

	STANDARD TARGET COMPOUND LIST (Soil)		NEW JERSEY TARGET COMPOUND LIST (Soil)		CT TARGET COMPOUND LIST (Soil)	
Analyte	**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**
Acenaphthylene	40-140	50	70-130	30	40-140	30
Acetophenone	14-144	50	70-130	30	40-140	30
Aniline	40-140	50	20-160	30	40-140	30
Anthracene	40-140	50	70-130	30	40-140	30
Atrazine	40-140	50	70-130	30		
Azobenzene	40-140	50	70-130	30		
Benzaldehyde	40-140	50	20-160	30		
Benzidine	10-66	50	20-160	30		
Benzo(a)anthracene	40-140	50	70-130	30	40-140	30
Benzo(a)pyrene	40-140	50	70-130	30	40-140	30
Benzo(b)fluoranthene	40-140	50	70-130	30	40-140	30
Benzo(e)pyrene	40-140	50				
Benzo(ghi)perylene	40-140	50	70-130	30	40-140	30
Benzo(k)fluoranthene	40-140	50	70-130	30	40-140	30
Benzoic Acid	10-110	50	20-160	30		
Benzyl Alcohol	40-140	50	20-160	30		
Biphenyl	54-104	50	70-130	30		
Bis(2-chloroethoxy)methane	40-117	50	70-130	30	40-140	30
Bis(2-chloroethyl)ether	40-140	50	70-130	30	40-140	30
Bis(2-chloroisopropyl)ether	40-140	50	70-130	30	40-140	30
Bis(2-Ethylhexyl)phthalate	40-140	50	70-130	30	40-140	30
Butyl benzyl phthalate	40-140	50	70-130	30	40-140	30
Caprolactam	15-130	50	20-160	30		
Carbazole	54-128	50	70-130	30	40-140	30
Chrysene	40-140	50	70-130	30	40-140	30
Dibenzo(a,h)anthracene	40-140	50	70-130	30	40-140	30
Dibenzofuran	40-140	50	70-130	30	40-140	30
Diethyl phthalate	40-140	50	70-130	30	40-140	30
Dimethyl phthalate	40-140	50	70-130	30	40-140	30
Di-n-butylphthalate	40-140	50	70-130	30	40-140	30
Di-n-octylphthalate	40-140	50	70-130	30	40-140	30
Diphenamid	40-140	50				
Fluoranthene	40-140	50	70-130	30	40-140	30
Fluorene	40-140	50	70-130	30	40-140	30
Hexachlorobenzene	40-140	50	70-130	30	40-140	30
Hexachlorobutadiene	40-140	50	70-130	30	40-140	30
Hexachlorocyclopentadiene	40-140	50	20-160	30	40-140	30
Hexachloroethane	40-140	50	20-160	30	40-140	30
Indeno(1,2,3-cd)Pyrene	40-140	50	70-130	30	40-140	30
Isophorone	40-140	50	70-130	30	40-140	30

	STANDARD TARGET COMPOUND LIST (Soil)		NEW JERSEY TARGET COMPOUND LIST (Soil)		CT TARGET COMPOUND LIST (Soil)	
Analyte	**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**	**Acceptance Criteria**	**Duplicate RPD**
Naphthalene	40-140	50	70-130	30	40-140	30
Nitrobenzene	40-140	50	70-130	30	40-140	30
NitrosoDiPhenylAmine(NDPA)/ Diphenylamine (DPA)	36-157	50	70-130	30	40-140	30
n-Nitrosodimethylamine	22-100	50	20-160	30		
n-Nitrosodi-n-propylamine	32-121	50	70-130	30	40-140	30
Parathion, ethyl	40-140	50	20-160	30		
P-Chloro-M-Cresol	26-103	50	70-130	30	30-130	30
Pentachloronitrobenzene	42-153	50			40-140	30
Pentachlorophenol	17-109	50	20-160	30	30-130	30
Phenanthrene	40-140	50	70-130	30	40-140	30
Phenol	26-90	50	20-160	30	30-130	30
Pyrene	35-142	50	70-130	30	40-140	30
Pyridine	10-93	50	20-160	30	40-140	30
Thionazin	40-140	50				
2-Fluorophenol	*25-120*		*30-130*		*30-130*	
Phenol-d6	*10-120*		*30-130*		*30-130*	
Nitrobenzene-d5	*23-120*		*30-130*		*30-130*	
2-Fluorobiphenyl	*30-120*		*30-130*		*30-130*	
2,4,6-Tribromophenol	*10-136*		*30-130*		*30-130*	
4-Terphenyl-d14	*18-120*		*30-130*		*30-130*	

TABLE 4 – Tailing Factor Calculation



Tailing Factor = $\frac{BC}{AB}$

Example calculation:

Peak Height = DE = 100mm
10% Peak Height = BD = 10mm
Peak Width at 10% Peak Height = AC = 23mm

AB = 11mm
BC = 12mm

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

Tailing factor for benzidine < 2.0

Tailing factor for pentachlorophenol <2.0

TABLE 5

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Primary Ion	Secondary Ion(s)
Acenaphthene	154	153, 152
Acenaphthylene	152	151, 153
Acetophenone	105	71, 51, 120
Aniline	93	66, 65
Anthracene	178	176, 179
Atrazine	200	202, 215
Azobenzene	77	182, 105
Benzaldehyde	105	77
Benzidine	184	92, 185
Benzo(a)anthracene	228	229, 226
Benzo(a)pyrene	252	253, 125
Benzo(b)fluoranthene	252	253, 125
Benzo(g,h,i)perylene	276	138, 277
Benzo(k)fluoranthene	252	253, 125
Benzoic acid	105	122, 77
Benzyl alcohol	79	77,108
Biphenyl	154	153,152
Bis (2-chloroethoxy) methane	93	95, 123
Bis (2-chloroethyl) ether	93	63, 95
Bis (2-chloroisopropyl) ether	45	77, 121
Bis (2-ethylhexyl) phthalate	149	167, 279
4-Bromophenyl phenyl ether	248	250, 141
Butyl Benzyl phthalate	149	91, 206
Caprolactam	55	85, 113
Carbazole	167	168, 166
4-Chloro-3-methylphenol	107	144, 142
2-Chloroaniline	127	129, 65
3-Chloroaniline	65	127, 129
4-Chloroaniline	65	127,129
2-Chloronaphthalene	162	127, 164
4-Chlorophenyl phenyl ether	204	206, 141
2-Chlorophenol	128	64,130
Chrysene	228	226, 229
Dibenzo(a,h)anthracene	278	139, 279
Dibenzofuran	168	139
1,2-Dichlorobenzene	146	148, 111

1,3-Dichlorobenzene	**146**	**148, 111**
1,4-Dichlorobenzene	**146**	**148, 111**
3,3'-Dichlorobenzidine	**252**	**254, 126**
2,4-Dichlorophenol	**162**	**164, 98**
Diethyl phthalate	**149**	**177, 150**

TABLE 5 (continued)

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Primary Ion	Secondary Ion(s)
3,3-Dimethylbenzidine	**212**	**211, 213**
Dimethyl phthalate	**163**	**194, 164**
2,4-Dimethylphenol	**107**	**121,122**
Di-n-butyl phthalate	**149**	**150, 104**
Di-n-octyl phthalate	**149**	**167, 43**
4,6-Dinitro-2-methylphenol	**198**	**51, 105**
O-Toluidine	**106**	**107, 77**
2-Ethylaniline	**106**	**121, 77**
2,4-Dimethylaniline	**121**	**120, 106**
2,3-Dimethylaniline	**106**	**121, 120**
3,4- Dimethylaniline	**121**	**120,106**
2,4,5-Trimethylaniline	**120**	**135, 134**
4-Chlorotoluidine	**106**	**141, 140**
2-Napthylamine	**143**	**115, 116**
2,4-Dinitrophenol	**184**	**107,91**
2,4-Dinitrotoluene	**165**	**63, 89**
2,6-Dinitrotoluene	**165**	**63, 89**
Diphenamide	**167**	**72, 165**
1,4-Dioxane	**88**	**58,43**
Ethyl parathion	**109**	**97, 291**
Fluoranthene	**202**	**101, 203**
Fluorene	**166**	**165, 167**
Hexachlorobenzene	**284**	**142, 249**
Hexachlorobutadiene	**225**	**223, 227**
Hexachlorocyclopentadiene	**237**	**235, 272**
Hexachloroethane	**117**	**201, 199**
Indeno(1,2,3-cd)pyrene	**276**	**138, 227**
Isophorone	**82**	**95, 138**
1-Methylnaphthalene	**115**	**141, 142**
2-Methylnaphthalene	**142**	**141**
2-Methylphenol	**108**	**107,90**
3/4-Methylphenol	**108**	**107,90**

Naphthalene	**128**	**129, 127**
2-Nitroaniline	**65**	**92, 138**
3-Nitroaniline	**138**	**92,65**
4-Nitroaniline	**138**	**65, 108, 92, 80, 39**
Nitrobenzene	**77**	**123, 65**

TABLE 5 (continued)

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Primary Ion	Secondary Ion(s)
2-Nitrophenol	**139**	**109, 65**
4-Nitrophenol	**65**	**109, 139**
n-Nitrosodimethylamine	**74**	**42,44**
n-Nitrosodi-n-butylamine	**84**	**57, 41, 116, 158**
n-Nitrosodi-n-propylamine	**70**	**42, 101, 130**
n-Nitrosodiphenylamine/Diphenylamine	**169**	**168, 167**
Pentachlorobenzene	**250**	**252, 108, 248, 215, 254**
Pentachloronitrobenzene	**237**	**142, 214, 249, 295, 265**
Pentachlorophenol	**266**	**264, 268**
Phenanthrene	**178**	**179, 176**
Phenol	**94**	**65, 66**
Pyrene	**202**	**200, 203**
Pyridine	**79**	**52**
1,2,4,5-Tetrachlorobenzene	**216**	**214, 179, 108, 143, 218**
2,3,4,6-Tetrachlorophenol	**232**	**131, 230, 166, 234, 168**
m-Toluidine	**106**	**107, 79**
1,2,4-Trichlorobenzene	**180**	**182, 145**
2,4,5-Trichlorophenol	**196**	**200,198**
2,4,6-Trichlorophenol	**196**	**198, 200**
Acenaphthene-d_{10} (IS)	**164**	**162, 160**
Chrysene-d_{12} (IS)	**240**	**120, 236**
1,4-Dichlorobenzene-d_4 (IS)	**152**	**150, 115**
Naphthalene-d_8 (IS)	**136**	**68**
Perylene-d_{12} (IS)	**264**	**260, 265**
Phenanthrene-d_{10} (IS)	**188**	**94, 80**
2-Fluorobiphenyl (Surrogate)	**172**	**171**
2-Fluoroophenol (Surrogate)	**112**	**64**
Nitrobenzene-d_5 (Surrogate)	**82**	**128, 54**
Phenol-d_6 (Surrogate)	**99**	**42, 71**
Terphenyl-d_{14} (Surrogate)	**244**	**122, 212**
2,4,6-Tribromophenol (Surrogate)	**330**	**62,141**

TABLE 6

REPORTED DETECTION LIMITS FOR SEMIVOLATILE ORGANIC COMPOUNDS*

Analyte	RDL (µg/L)	RDL (µg/Kg)
Acenaphthene	2	133.34
Acenaphthylene	2	133.34
Acetophenone	5	333.34
Aniline	2	133.34
Anthracene	2	133.34
Atrazine	10	666.67
Azobenzene	2	500
Benzaldehyde	5	333.34
Benzidine	20	1333.34
Benzo(a)anthracene	2	133.34
Benzo(b)fluoranthene	2	133.34
Benzo(k)fluoranthene	2	133.34
Benzo(ghi)perylene	2	133.34
Benzo(a)pyrene	2	133.34
Benzoic acid	50.0	3333.34
Benzyl alcohol	2	133.34
Biphenyl	2	366.67
Bis(2-chloroethyl)ether	2	133.34
Bis(2-chloroisopropyl)ether	2	133.34
Bis(2-chloroethoxy)methane	5.0	333.34
Bis(2-ethylhexyl)phthalate	3	200
4-Bromophenyl phenyl ether	2	133.34
Butyl benzyl phthalate	5.0	333.34
Caprolactam	10	666.67
Carbazole	2	166.67
2-Chloroaniline	2	na
3-Chloroaniline	10	na
4-Chloroaniline	5	333.34
p-Chloro-m-cresol (4-chloro-3-cresol)	2	133.34
2-Chloronaphthalene	2	133.34
2-Chlorophenol	2	133.34
4-Chlorophenyl phenyl ether	2	133.34
Chrysene	2	133.34
m/p-Methylphenol (3/4-methylphenol)	5.0	333.34
o-Methylphenol (2-methylphenol)	5.0	333.34

Dibenzo(a,h)anthracene	2	133.34
Dibenzofuran	2	133.34
Di-n-butylphthalate	5.0	333.34
1,2-Dichlorobenzene	2	133.34

TABLE 6 (continued)

REPORTED DETECTION LIMITS FOR SEMIVOLATILE ORGANIC COMPOUNDS*

Analyte	RDL (µg/L)	RDL (µg/Kg)
1,3-Dichlorobenzene	2	133.34
1,3-Dinitrobenzene	2	N/A
1,4-Dichlorobenzene	2	133.34
3,3-Dichlorobenzidine	5	333.34
2,4-Dichlorophenol	5	333.34
O-Toluidine	2	N/A
2-Ethylaniline	2	N/A
2,4-Dimethylaniline	2	N/A
2,3-Dimethylaniline	2	N/A
3,4-Dimetylaniline	2	N/A
2,4,5-Trimethylaniline	2	N/A
4-Chlorotoluidine	2	N/A
2-Napthylamine	2	N/A
2,6-Dichlorophenol	10.0	666.67
Diethyl phthalate	5.0	333.34
3,3-Dimethylbenzidine	4	500
2,4-Dimethylphenol	5	333.34
Dimethyl phthalate	5.0	333.34
4,6-Dinitro-o-cresol	10	666.67
2,4-Dinitrophenol	20	1333.4
2,4-Dinitrotoluene	5.0	333.34
2,6-Dinitrotoluene	5.0	333.34
Di-n-octylphthalate	5.0	333.34
Diphenamide	5	N/A
1,4-Dioxane	5	166.67
Ethyl Parathion	N/A	166.67
Fluoranthene	2	133.34
Fluorene	2	133.34
Hexachlorobenzene	2	133.34
Hexachlorobutadiene	2	133.34
Hexachlorocyclopentadiene	20	1333.34
Hexachloroethane	2	133.34
Indeno(1,2,3-cd)pyrene	2	133.34
Isophorone	5.0	333.34

1-Methylnaphthalene	2	166.67
2-Methylnaphthalene	2	133.34
Naphthalene	2	133.34
2-Nitroaniline	5.0	333.34

TABLE 6 (continued)

REPORTED DETECTION LIMITS FOR SEMIVOLATILE ORGANIC COMPOUNDS*

Analyte	RDL (µg/L)	RDL (µg/Kg)
3-Nitroaniline	5.0	333.34
4-Nitroaniline	5.0	333.34
Nitrobenzene	2	133.34
2-Nitrophenol	10.0	666.67
4-Nitrophenol	10.0	666.67
Nitrosodi-n-butylamine	10.0	666.67
n-Nitrosodimethylamine	2	133.34
n-Nitrosodiphenylamine/Diphenylamine	2	133.34
Nitrosodipiperidine	20.0	2000
n-Nitrosodi-n-propylamine	5.0	333.34
Pentachlorobenzene	20.0	1333.34
Pentachloronitrobenzene	10.0	150
Pentachlorophenol	10.0	666.67
Phenanthrene	2	133.34
Phenol	5.0	333.34
Pyrene	2	133.34
Piridine	5	666.67
1,2,4,5-Tetrachlorobenzene	10	666.67
1,2,4-Trichlorobenzene	5.0	333.34
2,4,5-Trichlorophenol	5.0	333.34
2,4,6-Trichlorophenol	5.0	333.34
2,3,4,6-Tetrachlorophenol	5.0	166.66
m-Toluidine	5	300

*** Note**: Reporting Limits are based on standard 8270 reporting list. RLs may vary for other reporting lists.

Table 7
Semivolatile Internal Standards with Corresponding
Target Compounds and Surrogates Assigned for Quantitation

1,4-dichlorobenzene-d4	Naphthalene-d8	Acenaphthene-d10	Phenanthrene-d10	Chrysene-d12	Perylene-d12
O-Toluidine	2-Ethylaniline	2-Naphthylamine	3,3-Dimethylbenzidine	3,3'-Dichlorobenzidine	Benzo(g,h,i)perylene
1,2,4-Trichlorobenzene	2,4-Dimethylaniline	2,3,4,6-Tetrachlorophenol	Anthracene	Benzo(a)Anthracene	Dibenzo(a,h)anthracene
1,2-Dichlorobenzene	3,4-Dimethylaniline	2,3,5,6-Tetrachlorophenol	Benzidine	Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
1,3-Dichlorobenzene	2,3-Dimethylaniline	2,4,6-Tribromophenol, surr	Benzyl butyl phthalate	Benzo(b)fluoranthene	
1,4-Dichlorobenezne	2,4,5-Trimethylaniline	2,4-Dinitrophenol	Carbazole	Benzo(k)fluoranthene	
2,4-Dichlorophenol	4-Chlorotoludine	2,4-Dinitrotoluene	Di-n-Butylphthalate	Bis(2-ethylhexyl) phthalate	
2,4-Dimethylphenol	1,2,4,5-Tetrachlorobenzene	3-Nitroaniline	Diphenamid	Chrysene	
2-Chloroaniline	1,2-Dichlorobenzene	4,6-Dinitro-2-methylphenol	Fluoranthene	Di-n-octylphthalate	
2-Chlorophenol	1,3-Dichlorobenzene	4-Bromophenyl-phenyl ether	n-Octadecane		
2-Fluorophenol, surr	1,4-Diclorobenzene	4-Chlorophenyl-phenyl ether	Parathion		
2-Methylphenol	1-chloror-2-nitrobenzene	4-Nitroaniline	Phenanthrene		
2-Nitrophenol	1-Methylnapthalene	4-Nitrophenol	Pyrene		
3-Methylphenol / 4-Methylphenol	2,4,5-Trichlorphenol	Acenaphthene	Terphenyl-d14, surr		
Acetophenone	2,4,6-Trichlorophenol	Atrazine			
Aniline	2,6-Dichlorophenol	Azobenzene			
Benzaldehyde	2,6-Dinitrotoluene	Dibenzofuran			
Benzyl Alcohol	2-Chloronaphthalene	Dichloran			
Bis(2-chloroethoxy)methane	2-Fluorobiphenyl, surr	Diethyl phthalate			
Bis(2-chloroethyl)ether	2-Methylnaphthalene	Fluorene			

Table 7 (cont.)
Semivolatile Internal Standards with Corresponding
Target Compounds and Surrogates Assigned for Quantitation

1,4-dichlorobenzene-d4	Naphthalene-d8	Acenaphthene-d10	Phenanthrene-d10	Chrysene-d12	Perylene-d12
bis(2-Chloroisopropyl)ether	2-Nitroaniline	Hexachlorobenzene			
Hexachloroethane	3-Choloroaniline	NDPA/DPA			
Isophorone	4-Chloro-3-Methylphenol	Pentachloronitrobenzene			
m-Toluidine	4-Chloroaniline	Pentachlorophenol			
n-Decane	Acenaphthylene				
Nitrobenzene	a-Terpineol				
Nitrobenzene-d5, surr	Benzoic Acid				
N-Nitrosodimethylamine	Biphenyl				
N-Nitrosodi-n-propylamine	Caprolactam				
Phenol	Dimethyl Phthalate				
Phenol-d6, surr	Hexachlorobutadiene				
Pyridine 1,4-Dioxane	Hexachlorocyclopentadiene				
Phenol-d6, surr	Naphthalene				

Table 8

Recommended Minimum Response Factor Criteria from Initial and Continuing Calibration Verification Using the Suggested Ions in Table 5

Analyte	MRF
Benzaldehyde	0.010
Phenol	0.800
Bis(2-chloroethyl)ether	0.700
2-Chlorophenol	0.800
2-Methylphenol	0.700
2,2'-Oxybis-(1-chloropropane)	0.010
Acetophenone	0.010
4-Methylphenol	0.600
N-Nitroso-di-n-propylamine	0.500
Hexachloroethane	0.300
Nitrobenzene	0.200
Isophorone	0.400
2-Nitrophenol	0.100
2,4-Dimethylphenol	0.200
Bis(2-chloroethoxy)methane	0.300
2,4-Dichlorophenol	0.200
Naphthalene	0.700
4-Chloroaniline	0.010
Hexachlorobutadiene	0.010
Caprolactam	0.010
4-Chloro-3-methylphenol	0.200
2-Methylnaphthalene	0.400
Hexachlorocyclopentadiene	0.050
2,4,6-Trichlorophenol	0.200
2,4,5-Trichlorophenol	0.200
1,1'-Biphenyl	0.010
2-Chloronaphthalene	0.800
2-Nitroaniline	0.010
Dimethyl phthalate	0.010
2,6-Dinitrotoluene	0.200
Acenaphthylene	0.900
3-Nitroaniline	0.010
Acenaphthene	0.900
2,4-Dinitrophenol	0.010
4-Nitrophenol	0.010
Dibenzofuran	0.800
2,4-Dinitrotoluene	0.200
Diethyl phthalate	0.010
1,2,4,5-Tetrachlorobenzene	0.010

Table 8 (cont.)

Recommended Minimum Response Factor Criteria from Initial and Continuing Calibration Verification Using the Suggested Ions in Table 5

Analyte	MRF
4-Chlorophenyl-phenyl ether	0.400
Fluorene	0.900
4-Nitroaniline	0.010
4,6-Dinitro-2-methylphenol	0.010
4-Bromophenyl-phenyl ether	0.100
N-Nitrosodiphenylamine	0.010
Hexachlorobenzene	0.100
Atrazine	0.010
Pentachlorophenol	0.050
Phenanthrene	0.700
Anthracene	0.700
Carbazole	0.010
Di-n-butyl phthalate	0.010
Fluoranthene	0.600
Pyrene	0.600
Butyl benzyl phthalate	0.010
3,3'-Dichlorobenzidine	0.010
Benzo(a)anthracene	0.800
Chrysene	0.700
Bis-(2-ethylhexyl)phthalate	0.010
Di-n-octyl phthalate	0.010
Benzo(b)fluoranthene	0.700
Benzo(k)fluoranthene	0.700
Benzo(a)pyrene	0.700
Indeno(1,2,3-cd)pyrene	0.500
Dibenz(a,h)anthracene	0.400
Benzo(g,h,i)perylene	0.500
2,3,4,6-Tetrachlorophenol	0.010

Table 9
Difficult analytes

Aniline

Benzaldehyde
Benzidine
Benzoic acid
Benzyl alcohol

Caprolactam
4-Chloroaniline
4-chloro-3-methylphenol (p-chloro-m-cresol)

3,3-Dimethylbenzidine
Dimethylphthalate
2,4 Dinitrophenol
4,6-dinitro-2-methylphenol (4,6-dinitro-o-cresol)

Hexachlorocyclopentadiene
Hexachloroethane

2-Methylphenol
3-Methylphenol/4-Methylphenol

2-nitroaniline
3-nitroaniline
4-nitroaniline
4-Nitrophenol
Nitrosodiphenylamine and diphenylamine (NDPA/DPA)
n-Nitrosodimethylamine

Parathion
Pentachloronitrobenzene
Pentachlorophenol
Phenol
Pyridine

Total and Amenable Cyanide

References: **Method 9010C / 9012B,** SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Revision 2 and Revision 3 2004

SM 4500CN-CEG. Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WEF. Standard Methods Online.

Method 10-204-00-1-A, Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218, 1994.

Method 9014 (Modified). SW-846, Test Methods for Evaluating Solid Waste: Physical / Chemical Methods, EPA SW-846, Update III, 1997.

1. Scope and Application

Matrices: This method is applicable to waters, liquids, solids, soils and sludges.

Definitions: See Alpha Laboratories Quality Manual Appendix A.

The following SOP is a reflux-distillation procedure used to extract soluble cyanide salts and many insoluble cyanide complexes from wastes and leachates. It is based on the decomposition of nearly all cyanides by a reflux distillation procedure using a strong acid and a magnesium catalyst. Cyanide, in the form of hydrocyanic acid (HCN) is purged from the sample and captured into an alkaline scrubber solution. The concentration of cyanide in the scrubber solution is then determined by flow injection analysis on a Lachat Analyzer.

This method was designed to address the problem of “trace” analyses (<1000ppm). The method may also be used for “minor” (1000ppm – 10,000ppm) and “major” (>10,000ppm) analyses by adapting the appropriate sample dilution. However, the amount of sodium hydroxide in the standards and the sample analyzed must be the same.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer

This method is restricted to use by or under the supervision of analysts experienced in the operation of the distillation unit and/or the Lachat Instrument, and in the interpretation of Lachat data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide concentration in the absorbing solution is then determined colorimetrically by Lachat flow injection analysis.

2.1 Method Modifications from Reference

The sample size used is 50mL. The Midi distillation unit has demonstrated the ability to achieve the same RDL using 50mL instead of 500mL sample volume. Refer to EPA Method 335.4.

Modification for Method 9014: An automated determination of cyanide using the Lachat instrument is used instead of manual spectrophotometric determination.

Modification for amenable cyanide: Analysis is not prepped under amber light.

3. Detection Limits

The Reported Detection Limit for aqueous samples is 0.005mg/L; soil and solid samples is 1mg/Kg.

4. Interferences

4.1 Instrumental

None.

4.2 Parameters

4.2.1 Interferences are eliminated or reduced by using the distillation procedure. However, chlorine and sulfide are interferences. Refer to Section 9.1.

4.2.2 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10mg/L and in conjunction with certain organic compounds.

4.2.3 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10mg/L were not found to interfere.

4.2.4 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations. Add anti-foaming agent to the sample during the distillation procedure (Section 9.2).

4.2.5 Carbonates and aldehydes are possible interferences

5. Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

The following chemicals have the potential to be highly toxic or hazardous. For detailed explanations consult the MSDS:

- Cyanide
- Sulfuric acid
- Pyridine
- Chloramine-T

6. Sample Collection, Preservation, and Handling

6.1 Sample Collection

Samples are collected in plastic or glass containers. All containers must be thoroughly cleaned and rinsed.

Oxidizing agents such as chlorine decompose most cyanides. Testing for chlorine must be done in the field prior to sample preservation.

6.2 Sample Preservation

Prior to preservation, samples must be tested for chlorine (Section 6.1).

Aqueous samples are preserved with 50% sodium hydroxide in the field to a pH $\geq$ 12 at the time of collection.

Samples and distillates are stored in the refrigerator at 4 ±2 °C.

6.3 Sample Handling

When properly preserved, cyanide samples are stored for up to 14 days prior to sample preparation steps.

Distillates must be analyzed within 14 days of distillation. Samples must be analyzed within 14 days of receipt.
Note: for MCP-TCN samples must be analyzed within 24h after distillation.

7. Equipment and Supplies

7.1 Cyanide Midi Distillation Unit: Lab Crest, BGL or comparable midi distillation unit. With reaction vessels, collection vessels, cold fingers and impingers.

7.2 pH paper: Range 1-14

7.3 Lead Acetate Paper

7.4 Vacuum source

7.5 50mL centrifuge tubes: New, plastic, with caps.

7.6 KI starch paper: Residual Chlorine sensitivity

7.7 Class A volumetric flasks: 25, 50, 100, 500 and 1000mL

7.8 Graduated cylinders: 50mL glass or plastic

7.9 Eppendorf pipettor or pipets: 0.5, 1, 2, and 5mL

7.10 Lachat 8500 Flow Analyzer: Including Quick Chem software, autosampler, pump and accessories.

7.11 Balance: Capable of weighing to 0.0001gram

7.12 Beakers: 100mL

7.13 Chiller

7.14 Stir plate

7.15 Stir bars

7.16 Dilu vials

8. Standards and Reagents

Reagent grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

8.1 Standards and Reagents for Distillation

8.1.1 Reagent Water: All references to water in this method refer to Deionized Water (DI) from Alpha's water treatment system.

8.1.2 Ascorbic Acid, $C_6H_8O_6$: Powder. Store at room temperature. Expires upon manufacturer's specified date.

8.1.3 Sodium hydroxide solution (1N), NaOH: In a 1L volumetric flask, dissolve 40g of NaOH. Bring to volume with DI water. Store at room temperature. Expires one month from date of preparation.

8.1.4 Sulfamic acid (0.4N), H_2NSO_3H: In a 1L volumetric flask, dissolve 40g H_2NSO_3H. Bring to volume with DI water. Store at room temperature. Expires 6 months from date of preparation.

8.1.5 Sulfuric acid (1:1), H_2SO_4: To a 1L volumetric flask, add 500mL DI water. Slowly and carefully add 500mL of concentrated H_2SO_4. Store at room temperature. Expires one month from date of preparation.

8.1.6 Magnesium chloride solution (2.5M), $MgCl_2 \cdot 6H_2O$: In a 1L volumetric flask, dissolve 510g of $MgCl_2 \cdot 6H_2O$. Bring to volume with DI water. Store at room temperature. Expires 6 months from date of preparation.

8.1.7 LCS, 1000ppm cyanide stock solution: Commercially available standard with a certificate of analysis and from a different source than the Lachat calibration standards. Purchased from Ricca, Catalog # 2543-32. Store refrigerated at 4 ± 2 °C. Expires upon manufacturer's specified date.

8.1.8 LCS 10ppm cyanide working solution: Pipet 1mL of 1000ppm cyanide stock solution(Section 8.1.7) into a 100mL volumetric flask. Add 10mL of 1N NaOH (Section 8.1.3). Bring to volume with DI water. Prepare each day of use.

8.1.9 1000ppm Stock Spiking Solution: 1000ppm cyanide standard available commercially with a certificate of analysis. This is from a different source than the LCS (8.1.7). Purchased from LabChem Inc., Catalog # LC13545. Store refrigerated at 4 ± 2 °C. Expires upon manufacturer's specified date.

8.1.10 10ppm Working Cyanide Spiking Solution: Pipet 1mL of the 1000ppm Stock Spiking Solution (Section 8.1.9) into a 100mL volumetric flask. Add 10mL 1N NaOH (Section 8.1.3). Bring to volume with DI water. Prepare fresh each day of use.

8.1.11 pH 4 Acetate Buffer solution: In a 500mL volumetric flask, dissolve 410g of sodium acetate trihydrate. Bring to volume with DI water. Adjust to pH of 4.5 with acetic acid (Section 8.1.13). Store at room temperature. Expires 6 months from date of preparation.

8.1.12 Lead Carbonate Powder, [Pb (CO3)]

8.1.13 LCS 0.5 ppm Cyanide Working Solution: Pipet 5mL of the 10ppm Working Cyanide Spiking Solution (Section 8.1.10) into a 100mL volumetric flask . Add 1mL of 10N NaOH (Section 8.1.16). Bring to volume with DI water. Prepare each day of use.

8.1.14 Concentrated Acetic Acid: Store at room temperature. Expires upon manufacturer's specified date.

8.1.15 Ottawa Sand or Boiling chips

8.1.16 Sodium hydroxide solution (10N), NaOH: In a 1L volumetric flask, dissolve 400g of NaOH. Bring to volume with DI water. Store at room temperature. Expires 6 months from date of preparation.

8.1.17 Total Cyanide SRM: ERA catalog # 541. Store in room temperature. Expires upon manufacturer's specified date.

8.1.18 Calcium Hypochlorite Solution: Dissolve 5g Ca(OCl)2 in 100mL Deionized water. Store in an amber colored bottle in the dark. Expires monthly.

8.2 Standards and Reagents for Lachat Analysis

8.2.1 Helium gas: To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in^2) through a helium degassing tube (Lachat part number 50100). Bubble He vigorously through the solution for one minute.

8.2.2 Reagent 1. Carrier, 0.1N Sodium Hydroxide: In a 1L plastic container add 10mL of 10N NaOH (Section 8.1.16). Bring to 1L volume with DI. Store at room temperature. Prepare fresh bi-weekly.

8.2.3 Reagent 2. Acetate Buffer, 2.68M: In a 1L volumetric flask, dissolve 163g spdium acetate trihydrate (acetic acid, sodium salt trihydrate, $CH_3CO_2NA•H_2O$) in approximately 800mL of water. Add 40mL of acetic acid to solution. Dilute to the mark and invert to mix. Store at room temperature. Prepare fresh monthly.

8.2.4 Reagent 3. Chloramine-T: Dissolve 2.0g chloramine-T hydrate in 500mL DI. Prepare fresh daily.

8.2.5 Reagent 4. Pyridine-Barbituric Acid Reagent: Under a fume hood, place 15g barbituric acid in a 1L beaker and add 100mL water, rinsing down the sides of the beaker to wet the barbituric acid. Add 75mL pyridine (C_5H_5N) while stirring and mix until the barbituric acid dissolves. Add the 15mL concentrated hydrochloric acid (12M HCl) and mix. Store at room temperature. Prepare fresh weekly.

8.2.6 0.5ppm Calibration standard: Pipet 5mL of the 10ppm working cyanide spiking solution (Section 8.1.10) into a 100mL volumetric flask. Bring to volume with 0.1N NaOH. Prepare each day of use.

8.2.7 0.2ppm Calibration standard: Pipet 2mL of the 10ppm working cyanide spiking solution (Section 8.1.10) into a 100mL volumetric flask. Bring to volume with 0.1N NaOH. Prepare each day of use.

8.2.8 0.1ppm Calibration standard: Pipet 1mL of the 10ppm working cyanide spiking solution (Section 8.1.10) into a 100mL volumetric flask. Bring to volume with 0.1N NaOH. Prepare each day of use. This calibration standard is also used as the Continuing Calibration Verification sample.

8.2.9 0.04ppm Calibration standard: Pipet 5mL of the 0.2ppm calibration standard (Section 8.2.7) into a 25mL volumetric flask. Bring to volume with 0.1N NaOH. Prepare each day of use.

8.2.10 0.02ppm Calibration standard: Pipet 1mL of the 0.5ppm calibration standard (Section 8.2.6) into a 25mL volumetric flask. Bring to volume with 0.1N NaOH. Prepare each day of use.

8.2.11 0.01ppm Calibration standard: Pipet 10mL of the 0.02ppm calibration standard (Section 8.2.10) and 10mL of 0.1N NaOH into a container and mix. Prepare each day of use.

8.2.12 0.004ppm Calibration standard: Pipet 5mL of 0.04ppm calibration standard (Section 8.2.9) into a 50mL volumetric flask. Bring to volume with 0.1N NaOH. Prepare each day of use.

8.2.13 0.1ppm ICV standard: Pipet 1mL of the 10ppm LCS cyanide working solution (8.1.8) into a 100mL volumetric flask. Bring to volume with 0.1N NaOH. Prepare each day of use.

9. Procedure

9.1 Screening for Chlorine and Sulfide Interference

9.1.1 Chlorine Interference

Oxidizing agents, such as chlorine, decompose most cyanides. Test by placing a drop of sample on a strip of potassium iodide (KI) - starch paper previously moistened with acetate buffer solution, pH 4. If positive indication is noted, then treat an aliquot of sample with Ascorbic Acid (Section 8.1.2). Repeat this test until the KI paper is negative. Immediately inform the Department Supervisor of this interference.

Manganese dioxide, nitrosyl chloride, etc., if present also may cause discoloration of the test paper.

9.1.2 Sulfide Interference
Oxidized products of sulfide convert CN- to SCN- rapidly, especially at high pH. Test for S^{-2} by placing a drop of sample on lead acetate test paper previously moistened with acetic acid buffer solution, pH 4 (Section 8.1.11). Darkening of the paper indicates presence of S^{-2}. Add powdered lead carbonate [Pb (CO3)] in 1g increments to the whole sample volume. Re-test with acetate paper. Repeat test until a drop of treated sample no longer darkens the acidified lead acetate test paper. Record in the sample prep logbook the amount of lead carbonate added to the sample.

9.2 Distillation

9.2.1 Add 50mL of shaken liquid sample, or 1gram of a well-homogenized solid sample and 50mL of DI, to the 50mL reaction vessel.

9.2.2 For the Liquid High LCS, fill one 50mL reaction vessel with 50mL DI. For the soil High LCS, add 1g Ottawa Sand (Section 8.1.15) and 50mL of DI. After the system has been charged with air, add 1mL of 10ppm LCS cyanide working solution (8.1.8) to the closed system. (Final concentration equals 0.2mg/L.)

For the Liquid Low LCS, fill one 50mL reaction vessel with 50mL of DI. For a soil Low LCS, add 0.2-0.3 g (depending on actual SRM stock concentration) of SRM (sec 8.1.17) and 50mL of DI. Record exact SRM weight. For liquid samples: After the system has been charged with air, add 0.5mL of 10ppm LCS cyanide working solution (Section 8.1.8) to the closed system. (Final concentration equals 0.1mg/L.) **Don't add liquid Cyanide Standard for soil samples!** Final LCS soil concentration will change based on SRM lot
Samples for Method 9010C/9012B: Prepare a LCS Duplicate along with the LCSs described above.

9.2.3 For the method blank for liquid samples, fill one 50mL reaction vessel with 50mL of DI. For the method blank for soil samples, fill a 50mL reaction vessel with 1g of Ottawa Sand (Section 8.1.15) and 50mL DI.

9.2.4 For the matrix spike, fill a 50mL reaction vessel with 50mL of sample that has been chosen to be spiked. For soil samples, use 1g of soil and add 50mL of DI water. After the system has been charged with air, add 1mL of 10ppm working cyanide spiking solution (8.1.10) to the closed system.

Samples for Method 9010C/9012B: Prepare a Matrix Spike Duplicate (MSD) in the same manner as the MS, as described above.

9.2.5 For the duplicate, fill a 50mL reaction vessel with a duplicate aliquot of 50mL, or 1g soil and 50mL DI water of a sample that has been chosen to be duplicated.

9.2.6 Into the receiver or scrubber tube add 5mL of a 1N NaOH solution and add 40mL of DI water.

9.2.7 Arrange tubes in the distillation unit noting in the logbook which sample is in which glassware. The glassware is numbered and consistently placed in the same position in the distillation unit.

9.2.8 Assemble the unit completely. Turn on the pump. There must be gas bubbling in each tube. Check to make sure all connections are tight and bubbles are flowing at an equal rate in each sample tube. If not, adjust flow rate with the knobs in front of each receiver tube and/or check lines to ensure they are not obstructed.

9.2.9 Add 5mL of 0.4N sulfamic acid (8.1.4) to each sample tube and rinse the closed 50mL reaction vessel with a squirt of DI. No residue is to be left of the vessel wall.

9.2.10 Add 5mL of 1:1 H_2SO_4 (8.1.5) to each sample tube and rinse the closed 50mL reaction vessel with a squirt of DI. No residue is to be left on the vessel wall. Turn on the heat. Samples are to come to a boil on all of the midi-still units.

9.2.11 After 2 minutes of heating, add 2mL of 2.5M $MgCl_2$ Solution (8.1.6) to each sample tube, followed by a rinse with DI. If foaming occurs, an additional 2mL of $MgCl_2$ Solution may be added. If foaming continues, stop the distillation for that sample and reduce the sample size by 2 – 5x (as determined by the severity of the foaming). Contact the Inorganics Supervisor for guidance.

9.2.12 Turn on the chiller.

9.2.13 Set the timer-dial on the distillation unit to “110”.

9.2.14 After 110 minutes the unit will shut off; leave the chiller running for an additional 30 minutes while the tubes cool down.

9.2.15 Pour contents of the scrubber tube into a new, labeled, centrifuge tube (Section 7.5). Carefully rinse the scrubber tube with DI water and add rinseate to the centrifuge tube to bring to 50mL volume. Cap and refrigerate for later analysis by the Lachat Instrument.

9.3 Initial Calibration of Lachat Instrument

9.3.1 Allow 15 minutes for heating unit to warm up to 60 °C.

9.3.2 Prepare a series of 7 calibration standards (Sections 8.2.6 – 8.2.12) and a 0.1N NaOH blank. Alternatively, calibration standards may be prepared by auto-diluting a 0.5ppm calibration standard (Section 8.2.6). Perform this function per the Lachat manufacturer’s instructions for the Quick Chem 8500.

9.3.3 Set up manifold as shown in Table 1.

9.3.4 Input data system parameters as shown in Table 2.

9.3.5 Place standards and blank in the autosampler, per the manufacturer’s instructions. Input the information required by the data system, such as concentration, replicates and QC scheme.

9.3.6 Inject the standards, per the manufacturer’s instructions.

9.3.7 Prepare a standard curve by plotting instrument response against standard concentration values. A calibration curve is fitted to the calibration solution

concentration/response data using the computer. The calibration coefficient of the curve must be greater than or equal to 0.995 before sample analysis can begin.

Calibration coefficient will be calculated using Lachat software. All calibration points are back calculated by Lachat software and should be within 10% from true concentration, except 2 lowest points of calibration curve. %recoveries for low range will be wider, but shouldn't exceed 100% and correlation coefficient will not be worse then 0.995.

9.4 Standardization (Continuing Calibration Verification)

9.4.1 After the calibration has been established, it must be verified by the analysis of an Initial Calibration Verification Standard (ICV) (Section 8.2.13). The ICV of 0.1ppm must be made from a different source than the calibration standards. If the measurements exceed ±10% of 0.1ppm, the analysis is terminated. See Section 10.6 for Corrective Actions.

9.4.2 A Blank and a Continuing Calibration Verification (CCV) sample (Section 8.2.8) are analyzed after every 10 injections. The CCV measurements cannot exceed ±10% of the CCV value of 0.1ppm and the blank result must be less than the reporting limit of 0.005 mg/L. See Section 10.6 for CCV Corrective Actions and Section 10.2 for Blank corrective actions.

9.5 Lachat Analysis

9.5.1 Following initial calibration and standardization, (Section 9.3 and 9.4), place the samples in the autosampler, per the manufacturer's instructions. Input the information required by the data system, such as concentration, replicates and QC scheme.

9.5.2 Inject the samples, per the manufacturer's instructions.

9.5.3 The data system calculates sample concentration using the regression equation. Results are mg/L for Aqueous samples and mg/Kg for soil and solid samples.

9.5.4 If sample concentrations are greater than the highest calibration standard, the distilled sample is diluted with 0.1N sodium hydroxide (NaOH) diluent (Section 8.2.2), and reanalyzed. When the automated diluter is used, 0.1N NaOH is also used. **Do not dilute distilled samples or standards with DI water.**

9.6 Preventative Maintenance

Preventative maintenance is recorded in the instrument maintenance logbook and is performed on the Lachat instrument as follows:

Daily:

1) Clean the autosampler
2) Clean the surfaces on the auto-dilutor
3) Prime the dilutor with fresh DI water
4) Clean the pump surfaces
5) Clean the detector with DI and dry with Kim-Wipes
6) Clean the instrument surfaces with DI, wipe clean with a paper towel

Bi-weekly:

1) Clean the injection ports with DI. Take apart the injection valve and inspect it for corrosion. Make sure that the valve connectors are tight and the o-rings are not worn. If the O-rings look worn replace with new ones.

Monthly:

1) Using DI water, clean the unions and the tees that are associated with the manifold.
2) Delete Temporary files on the computer

Every 6 months:

1) Replace the o-rings in the injection valve.
2) Replace the o-rings in the manifold
3) Back up the files on the computer

9.7 Calculations

9.7.1 The Lachat data system calculates sample concentration using the regression equation.

9.7.2 Report only those values that fall between the lowest and the highest calibration standards.

9.7.3 Report results in mg CN/L for liquids and in mg CN/kg for soils.

9.8 Amenable Cyanide Prep

9.8.1 Add 25mL, or 1g and 25mL of DI (8.1.1), to a 100mL beaker with a stir bar.

9.8.2 Add 1mL of 10ppm LCS cyanide working solution (8.1.8) to beaker.

9.8.3 Prep one sample in duplicate.

9.8.4 Add 1-2mL of calcium hypochlorite solution (8.1.18) to all samples and QC under the hood.

9.8.5 Check for the presence of chlorine by placing a drop of the sample on a KI-starch paper (7.6). It should turn blue if there is sufficient chlorine.

9.8.6 Check samples every 15 minutes for one hour for the presence of chlorine and add more calcium hypochlorite if needed.

9.8.7 After one hour of digesting, add ascorbic acid (8.1.2) until KI strip no longer turns blue.

9.8.8 Bring sample volume up to 50mL and distill following steps 9.2.6 thru 9.2.15.

10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation.

10.1 Demonstration of Capability

Refer to Alpha SOP/ 1734 and 1739 for DOC information.

10.2 Blank

A minimum of one method blank is distilled and analyzed per batch of 20 or less samples. The Method Blank is utilized to determine if contamination or any memory effects are occurring. (Section 9.2.1) The blank result must be less than the reporting limit of 0.005 mg/L for liquids and 1 mg/kg for soils. If the blank result is outside of acceptance criteria, it is injected another time. If failure continues, sample analysis is terminated and the source of the problem is found and corrected. All samples analyzed since the last acceptable blank analysis must be reanalyzed.

10.3 Laboratory Control Samples (LCS) / Laboratory Control Sample Duplicate (LCSD)

Distill and analyze two LCSs per batch of 20 samples. A Low LCS is analyzed at 0.1mg/L and a high LCS is analyzed at 0.2mg/L. (Section 9.2.2)

LCS measurements for Method SM 4500 CN-CE must be within ±10%. For Method 9010C/9012B, the LCS measurements must be within ± 15% for liquids and +/- 20% for soils.

Samples for Method 9010C/9012B: LCSDs are distilled and analyzed along with the LCSs, as described above. The RPD between LCS and LCSD must be ≤ 20% for liquids and ≤35% for soils.
For soil samples: LCS and LCSD recovery must be within vendor specified acceptance criteria (it will be different for different lots of SRM)

If any LCS fails acceptance criteria for either % Recovery or RPD, analysis is terminated and samples are redigested and analyzed.

10.4 Matrix Spike

Distill and analyze one spike per batch of 20 samples. For Method 9010C/9012B distill and analyze one spike per batch of 10 samples.
For Method 9010C/9012B, the % Recovery must be within ±20% for liquids and ±35% for solids. For SM 4500CN-CE, the % Recovery must be within ±10%. (Section 9.2.4).

Samples for Method 9010C/9012B: A Matrix Spike Duplicate (MSD) is distilled and analyzed along with the MS, as described above. The RPD between MS and MCSD must be ≤ 20% for liquids and ≤35% for soils.

10.5 Duplicates

Analyze one duplicate sample for every 20 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process. (Section 9.2.5)

The RPD must be 20% or less for liquids and 35% or less for soils and solids. See Section 12 for Corrective Action if these criteria are not met.

10.6 Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

The Initial Calibration Verification Standard (ICV) (Section 8.2.13) is analyzed immediately following the calibration to verify the curve. If the measurements exceeds ±10% of 0.1ppm, the analysis is terminated and recalibration must occur. An acceptable result for the ICV must be obtained prior to any sample analysis.

The Continuing Calibration Verification Standard (CCV) (Section 8.2.8) is analyzed after every 10 injections. The CCV measurements cannot exceed ±10% of the of 0.1ppm. If the CCV is not within acceptance criteria, the standard is injected again. If failure continues, sample analysis is terminated and the source of the problem is found and corrected. All samples analyzed since the last acceptable calibration verification must be reanalyzed.

10.7 Control Limits

Refer to SOP/ 1734.

10.8 Analytical Sequence

The analytical sequence is:

- Screening of samples for chlorine and sulfide
- Prep of amenable cyanide, if needed
- Distillation:
    - Samples
    - LCS Low
    - LCS High
    - Blank
    - Matrix Spike
    - Duplicate
- Analysis:
    - Calibration and Standardization of Lachat Instrument
    - CCV
    - CCB
    - ICV
    - ICB
    - 10 samples
    - CCV
    - CCB
    - 10 samples
    - CCV
    - CCB
    - Calculation of sample cyanide concentration

11. Method Performance

Refer to SOP/ 1732 for MDL/LOD/LOQ information. Refer to SOP/ 1734 and 1739 for DOC information.

12. Corrective Actions

Holding time exceedence and improper preservation are noted on the nonconformance report form. The analyst narrates the nonconformance when the project is turned in for review. The narration must state what the nonconformance was and any corrective action taken.

Perform routine preventative maintenance according to Section 9.6. Record all maintenance in the instrument logbook. Notify the Department Manager if the instrument problems are not routine in nature. The Department Manager determines whether the problem can be corrected with in-house technical staff or if the instrument vendor should be contacted to schedule service. All service calls are documented in the Instrument logbook, and a copy of the service report is given to the Department Manager.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. If any part of batch quality control does not meet acceptance criteria, the Department Manager is notified. If enough sample remains and holding time has not expired, then the batch is redistilled and reanalyzed. If there is not sufficient sample remaining to allow redistillation, then that analysis is repeated and both sets of data are reported with the nonconformance narrated on the final report.

If either the ICV, ICB, Method Blank, LCS, LCSD, CCV, or CCB recovery falls outside the designated acceptance range, the laboratory performance is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form.

Immediate corrective action for a failing CCV/CCB includes reanalyzing the failing standard. If the standard passes the second time then the analysis may be continued. The raw data is noted. If the standard fails again, the problem must be found and corrected. The CCV/CCB standard is remade and reanalyzed. If the standard passes, all samples analyzed since the previous passing standard are reanalyzed. The raw data is noted and all data associated with the failing standard must have one line drawn through the data, indicating its unusability.

If the standard fails after instrument maintenance, the instrument is recalibrated. A new ICV/ICB is performed, and all samples analyzed since the previous passing CCV/CCB are reanalyzed.

If following reanalysis of the LCS, it is found to still be outside acceptance criteria, the entire sample batch must be redistilled and reanalyzed. If the %RPD between the LCS/LCSD fails after reinjection, then the entire sample batch must be redistilled and reanalyzed.

If the Method Blank fails it is re-poured and reinjected. If failure continues, the associated sample data is evaluated as follows: Sample results below the detection limit may be reported with a narrative included. If samples have positive results, and the results are greater than 10x the concentration found in the method blank, the data may be reported with a narrative included. Any positive samples with results less than 10x the concentration found in the method blank must be redistilled and reanalyzed.

If the Matrix Spike recovery does not meet acceptance criteria, and the LCS recovery is acceptable, matrix interference may be assumed. The associated data may be reported with a narrative included.

If sample Duplicates are outside of the acceptance criteria, the analyst examines the sample for homogeneity. If the sample is not homogenous, this is narrated on the final report. Clean, homogenous samples are redistilled and reanalyzed within holding time.

Sample nonconformance regarding a Matrix Spike recovery or a duplicate %RSD is narrated on the final report along with the corrective action(s) taken.

13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

14. Waste Management

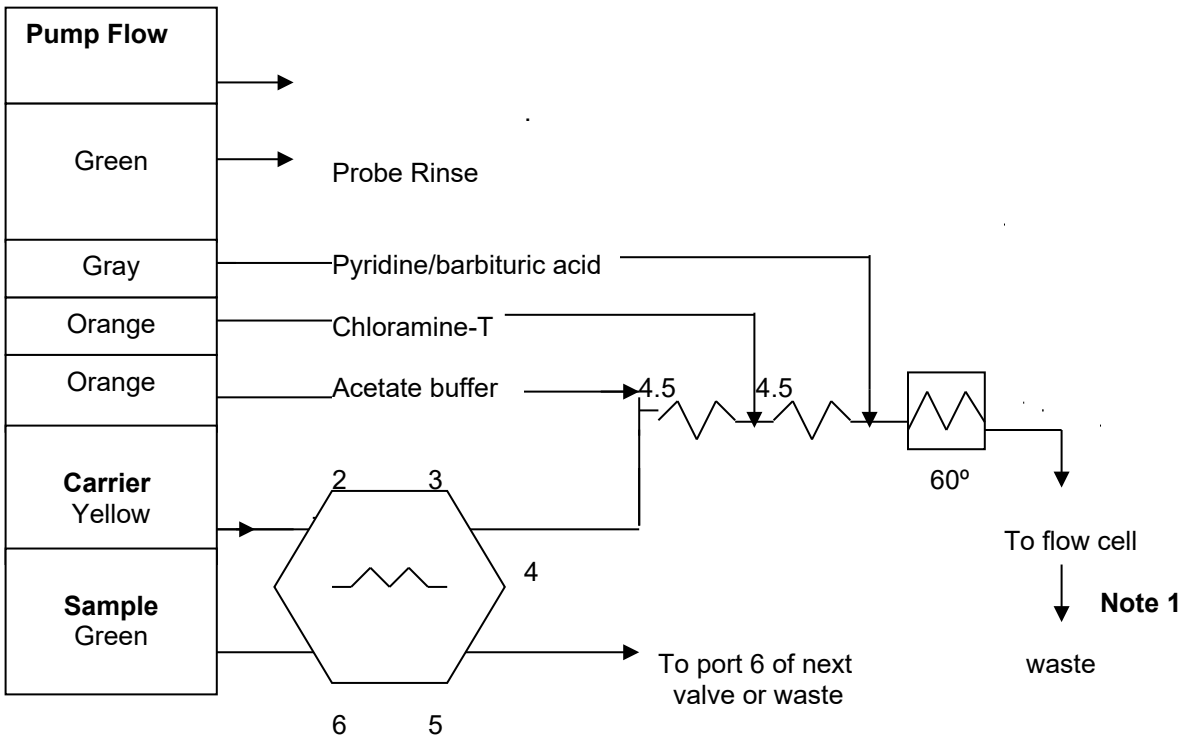
See Chemical Hygiene Plan for waste handling and disposal.

15. Attachments

TABLE 1: Cyanide Manifold Diagram

TABLE 2: Data System Parameters for QC 8500

TABLE 1
Cyanide Manifold Diagram



Sample Loop = 150cm x 0.8mm i.d. Interference Filter = 570nm
QC8000 Sample loop = 150cm x 0.8mm i.d.

CARRIER is 0.1 N sodium hydroxide solution.

All manifold tubing is 0.8mm (0.030 in) i.d. This is 5.2µL/cm.

4.5 is 70.0cm of tubing on a 4.5cm coil support

APPARATUS: An injection valve, flow cell, a 10mm path length flow cell, and a colorimetric detector module are required.

The box  shows 650cm of tubing wrapped around the heater block at the specified temperature.

Note 1: 2 meter back pressure loop, 0.52mm i.d.

TABLE 2
Data system Parameters for QC 8500

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample Throughput: 65 samples/hour, 55 s/sample
Pump Speed: 35
Cycle Period: 55

Analyte Data:

Concentration Units: mg CN^-/L
Peak Base Width: 60.5 s
% Width Tolerance: 100
Threshold: none
Inject to Peak Start: 55 s
Chemistry: Direct

Calibration Data:

Levels	1	2	3	4	5	6	7	8
Concentration ug/50mL	25	10	5	2	1	0.5	0.2	0

Calibration Fit Type: 1st Order Polynomial
Calibration Rep. Handling: Replace
Weighting Method: 1/X
Concentration Scaling: None
Force Through Zero: No

Sampler Timing:

Min. Probe in Wash Period: 14 s
Probe in Sample Period: 13 s

Valve Timing:

Load Time: 0.0 s
Load Period: 9 s
Inject Period: 20 s

Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

References: **Method 8260C**, SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, 2006.

Method 5035A, SW-846, Closed System Purge & Trap and Extraction for Volatile Organics in Soil and Waste Samples. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, Draft Revision I, July 2002.

Method 5030B, Purge & Trap for Aqueous Samples. SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, December, 1996.

Method 5030C, Purge & Trap for Aqueous Samples. SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update IV, May, 2003.

1. Scope and Application

Matrices: Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

Definitions: Refer to Alpha Analytical Quality Manual.

The following compounds may be determined by this method:

8260C LIST OF ANALYTES		
Dichlorodifluoromethane	Carbon tetrachloride	Isopropylbenzene
Chloromethane	1,2-Dichloroethane	1,4-Dichloro-2-butane
Vinyl chloride	Benzene	1,1,2,2-Tetrachloroethane
Chloroethane	Trichloroethene	Trans-1,4-dichloro-2-butene
Bromomethane	1,2-Dichloropropane	1,2,3-Trichloropropane
Trichlorofluoromethane	Bromodichloromethane	n-Propylbenzene
Ethyl ether	Dibromomethane	Bromobenzene
Acetone	4-Methyl-2-pentanone	2-Chlorotoluene
1,1-Dichloroethene	cis-1,3-Dichloropropene	1,3,5-Trimethylbenzene
Carbon disulfide	Toluene	4-Chlorotoluene
Methylene chloride	Trans-1,3-dichloropropene	Tert-butylbenzene
Acrylonitrile	Ethyl-methacrylate	1,2,4-Trimethylbenzene
Methyl-tert-butyl ether	1,1,2-Trichloroethane	Sec-butylbenzene
Trans-1,2-dichloroethene	2-Hexanone	p-Isopropyltoluene
1,1-Dichloroethane	1,3-Dichloropropane	1,3-Dichlorobenzene
Vinyl acetate	Tetrachloroethene	1,4-Dichlorobenzene
2-Butanone	Chlorodibromomethane	n-Butylbenzene
2,2-Dichloropropane	1,2-Dibromoethane	1,2-Dichlorobenzene
Cis-1,2-dichloroethene	Chlorobenzene	1,2-Dibromo-3-chloropropane
Chloroform	1,1,1,2-Tetrachloroethane	1,2,4-Trichlorobenzene
Bromochloromethane	Ethyl benzene	Hexachlorobutadiene
Tetrahydrofuran	p/m Xylene	Naphthalene
1,1,1-Trichloroethane	o Xylene	1,2,3-Trichlorobenzene

8260C LIST OF ANALYTES (continued)		
1,1-Dichloropropene	Styrene	Bromoform
Acrolein	2-Chloroethylvinyl ether	Ethanol
Cyclohexanone	Ethyl acetate	1,3,5-Trichlorobenzene
Iodomethane	Methyl methacrylate	Tert-amyl methyl ether
Di-isopropyl ether	n-Butanol	1,4-Dioxane
Ethyl Tert-Butyl Ether	Pentachloroethane	Isopropyl Alcohol (IPA)
Hexane	n-Propyl bromide	

There are various techniques by which these components may be introduced into the GC/MS system. Purge-and-trap, by Methods 5030C (aqueous samples) and 5035A (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. One technique is direct injection of an aqueous sample (concentration permitting).

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the gas chromatograph/mass spectrometers and in the interpretation of mass spectra and their use as a quantitative tool. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability.

2. Summary of Method

The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection. The analytes are introduced to a narrow-bore capillary column for analysis. The Gas Chromatograph (GC) is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the GC.

Analytes eluted from the capillary column are introduced into the mass spectrometer via a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard, comparing sample response to the calibration standards.

2.1 Method Modifications from Reference

None.

3. Reporting Limits

Table 1 lists our typical reporting limits.

4. Interferences

4.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be free from contamination under the conditions of the analysis. Running laboratory reagent blanks as described in Section 10.3 and 9.1

demonstrates the system is free of contamination. The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system must be avoided.

4.2 Sample contamination occurs by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A trip blank or a field reagent blank prepared from reagent water and carried through the sampling and handling protocol serves as a check on such contamination.

4.2.1 Storage blanks shall be analyzed if contamination is suspect. If contamination is confirmed by positive detections in the sample storage blanks, all data from samples contained in the relative refrigerator or freezer shall be evaluated for possible contamination. If the samples contain suspected contamination, the Client Services department shall be notified in order to contact the necessary clients regarding the contamination. Samples shall be reanalyzed if so desired by the client. If suspected contamination is not confirmed by storage blanks, no further action shall be pursued concerning said blanks. It is recommended that further action be taken to determine the possible cause of suspected contamination.

4.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. Whenever a highly concentrated sample is being encountered, it should be followed by an analysis of reagent water (instrument blank) to check for potential contamination. If carry-over is suspected, then numerous instrument blanks may be required; additionally all affected samples are rerun for confirmation. In case of severe contamination, preventive maintenance of the entire system may be required.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5.1 Lab coats, safety glasses, and gloves must be worn when handling samples, standards, or solvents.

5.2 All stock solution standard preparation must be performed in the volatiles hood. Initial calibration, continuing calibration, laboratory control sample and client sample dilutions do not need to be performed in the hood.

5.3 All expired standards must be placed into the waste bucket in the lab, for future disposal. The container must be labeled properly with hazard warning labels indicating the container contents.

5.4 Bottles containing Methanol must be stored in the flammables cabinet.

6. Sample Collection, Preservation, Storage, Shipping and Handling

6.1 Sample Collection and Preservation

6.1.1 Aqueous Samples

Grab samples are collected in standard 40mL amber glass screw-cap vials with Teflon lined silicon septa (VOA vial). Two or more VOA vials should be filled per sample location. EPA Method 8260 requires that samples be acidified to eliminate the possibility of biological degradation. Unless otherwise directed for project-specific reasons, all VOA vials are delivered to the client with approximately 2 – 4 drops of 1:1 HCl added to the vial, which is sufficient to adjust the pH of the sample to < 2. Prepared trip blanks are provided to the client to accompany field samples for QC purposes.

Fill the sample vial to the point of overflowing so that no headspace is contained within. Samples must be introduced into the vials gently to reduce agitation, which might drive off volatile compounds or cause loss of the HCl preservative.

Seal the bottle so that no air bubbles are in the VOA vial. If preservative has been added, shake vigorously for one minute. Invert the bottle and tap to check for air bubbles. Recollect the samples if any air bubbles are present.

Maintain the hermetic seal on the VOA vial until time of analysis.

6.1.2 Soil Samples

The recommended sampling method for soil samples is EPA 5035A. Method 5035A provides for two distinct sampling procedures, depending on the required reporting limits and suspected or known concentration levels of target analytes. These methods are referred to as the High Level and Low Level methods. Both are listed below, but depending on the samples only one of the methods may be required. If concentration levels are unknown, it is recommended that samples be collected using both procedures. The Lab will analyze the high level sample first, followed by the low level sample if the results from the high level analysis show that the sample is clean or contains analytes at low levels. The typical reporting levels of the two methods are listed in Table 1.

6.1.2.1 High Level Soil Samples

Collect sample in a standard 40mL amber glass screw-cap vial with Teflon lined silicon septa (VOA vial). The vial is provided containing 15mL of Purge and Trap Grade methanol, and is labeled and weighed prior to addition of sample. Record the weight of the vial with methanol on the vial label. Prepared trip blanks are provided to the client to accompany field samples for QC purposes.

Approximately 15g of soil is added to the vial in the field, making sure that the sample is completely covered by the methanol.

Maintain the hermetic seal on the VOA vial until the time of analysis.

An additional sample of the soil must also be obtained (without methanol) to be used for the determination of soil moisture content to allow for the calculation of the dry weight results, and to calculate the methanol dilution effect. (See Sections 11.1.2.2.2 and 11.1.2.2.3)

6.1.2.2 Low Level Soil Samples

Collect sample in a standard 40mL amber glass screw-cap vials with Teflon lined silicon septa (VOA vial). Two samples should be taken per sample location. Vials are provided containing a magnetic stirring bar and 5 mL of either 200g/L sodium bisulfate solution or water, prepared by a certified vendor. These vials are labeled and weighed prior to addition of sample. Record the weight of the vial with the stirring bar and preservative on the vial label.

Approximately 5g of soil is added to the vial in the field, making sure that the sample is completely covered by the sodium bisulfate solution or water.

Maintain the hermetic seal on the VOA until the time of analysis.

6.2 Sample Handling and Storage

Document client specific sample handling, preservation and collection criteria in the project file. The laboratory Log-in staff documents sample temperature at the time of receipt.

Record deviations from this SOP or client specific criteria on the chain of custody form.

Record holding time exceedence, improper preservation and observed sample headspace on the nonconformance report form.

6.2.1 Aqueous Samples

Ice or refrigerate all samples from the time of collection until analysis, maintaining the sample temperature between 1 and 4 °C. Sample receiving personnel note on the sample delivery group form when samples received at the laboratory are not within the temperature criteria. If more than one vial is received for a sample the vials are stored in separate refrigerators. Storing the vials apart provides a useful check if laboratory contamination of a sample is suspected. Samples must be analyzed within 14 days of collection. Unpreserved samples requiring aromatic analysis must be analyzed within 7 days of collection.

6.2.2 High Level Soil Samples

Ice or refrigerate all samples from the time of collection until analysis, maintaining the sample temperature between 2 and 6 °C. Sample receiving personnel note on the nonconformance report form when samples received at the laboratory are not within the temperature criteria.

6.2.3 Low Level Soil Samples

Ice or refrigerate samples preserved with water or sodium bisulfate from the time of collection until analysis, maintaining the sample temperature between 2 and 6 °C. Samples preserved with water are to be immediately frozen after sampling. Sample receiving personnel note on the nonconformance report form when samples received at the laboratory are not within the temperature criteria.

6.3 Sample Shipping

Samples requiring shipment to the laboratory are shipped in ice-packed coolers via an overnight delivery service in accordance with applicable Department of Transportation regulations.

7. Equipment and Supplies

7.1 Purge and Trap System (For Aqueous samples and High Level Soils): The purge-and-trap system consists of two separate pieces of equipment: a purging device (autosampler) (Varian Archon/8100, Tekmar Solatek, EST Centurion) coupled to the desorber (concentrator) (Tekmar Velocity or EST Encon).

7.1.1 Purge gas = Helium, analytical grade (99.999%).

7.1.2 The purging device is configured with 25 mL sample purge tubes, and the helium purge gas is introduced at the bottom of the water column as finely divided bubbles

7.1.3 The trap used in the desorber is typically a Supelco "K" trap. Different traps may be used if equivalent performance is demonstrated.

7.1.4 The desorber is capable of rapidly heating the trap to 260^{o}C. The trap is not heated above manufacturer's specifications

7.2. Purge and Trap System (For Low Level Soil Samples): The purge and trap system consists of two separate pieces of equipment: a purging device (autosampler) coupled to the desorber (concentrator) (Varian Archon/8100, Tekmar Solatek, EST Centurion with EST Encon, Tekmar Velocity, or equivalents).

7.2.1. Purge gas = Helium, analytical grade (99.999%).

7.2.2. The autosampler purging device is a closed system, designed to accept the 40mL VOA vials. The VOA vial, containing the soil sample, water (or sodium bisulfate), and stirring bar is placed into the autosampler tray. The instrument automatically adds reagent water, internal standards, and surrogates to the unopened VOA vial. The vial is heated to 40 °C, and the helium purge gas is introduced into the aqueous portion to purge the volatile components onto the trap.

7.2.3. The trap used in the desorber is typically a Supelco "K" trap. Different traps may be used if equivalent performance is demonstrated.

7.2.4. The desorber is capable of rapidly heating the trap to 260 °C. The trap is not heated above manufacturer specifications.

7.3 Gas Chromatography/Mass Spectrometer/Data System:

7.3.1 Gas Chromatograph, Agilent 6890/7890 or equivalent: An analytical system complete with a temperature-programmable gas chromatograph with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases. The capillary column is directly coupled to the source of the GC/MS system.

7.3.2 Typical Gas Chromatographic Columns:

7.3.2.1 Column 1: Restek 502.2, 40 meter, 0.18mm ID, or equivalent.

7.3.2.2 Column 2: Restek RTX-VMS, 30 meter, 0.25mm ID, or equivalent

7.3.3 Mass Spectrometer, Agilent 5973/5975/5978 or equivalent: Scanning from 35 to 300 amu every 2 seconds or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the

criteria in Table 3, when 50ng of the GC/MS tuning standard (BFB) are injected through the GC. For all SIM analysis, the mass spectrometer must also be able to acquire data in a dual acquisition mode (SIM and full scan).

7.3.4 Data System: Hewlett-Packard EnviroQuant software is used for data acquisition, and allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.

Thruput Target 4.12 software or Enviroquant E.02.02 (or equivalent) is used for data processing, and allows searching of any GC/MS data file for ions of a specified mass, and plotting such ion abundances versus time or scan-number.

The most recent version of the EPA/NIST Mass Spectral Library is loaded onto the Target / Enviroquant data system.

7.4 Wiretrol or Micro syringes: 10µL - 1,000µL.

7.5 Syringes: 5mL, 10mL, or 25mL, glass with Luerlock tip.

7.6 Balances: Top-loading**,** capable of weighing 0.01g.

7.7 Vials: 2mL, 4mL.

7.8 Disposable Pipets.

7.9 Volumetric Flasks: Class A, appropriate sizes, with ground-glass stoppers.

7.10 Eppendorf Pipets

8. Reagents and Standards

Reagent grade organic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all organic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Great care must be taken to maintain the integrity of all standard solutions. Standards in methanol are stored at –10ºC or less, in amber vials with PTFE-lined screw-caps.

8.1 Organic-free Reagent Water:

All references to water in this method refer to organic-free reagent water, which is tap water passed through activated carbon and air bubbled through.

8.2 Methanol:

Purge and Trap Grade or equivalent. Store in flammables cabinet.

8.3 Stock Solutions:

All stock standard solutions are purchased from commercial vendors as ampulated certified solutions. When an ampulated stock solution is opened, it is transferred to a labeled amber screw-cap vial with minimal headspace. The expiration date of the stock solution is either the vendor specified expiration date or 6 months from the date the ampule was opened, whichever is sooner. Typical stock standard concentrations are listed in Table 4.

8.4 Intermediate Standards: Intermediate standards are prepared volumetrically by diluting the appropriate stock standard(s) with methanol. Initial Calibration solutions expire 2 months from the date of preparation, or sooner if daily continuing calibration checks do not achieve the method acceptance criteria. If the Intermediate Standards are used as a second source to verify a valid Initial Calibration solution, there is no expiration date.

8.4.1 Internal Standard Solutions:

The internal standards are Fluorobenzene, Chlorobenzene-d_5, and 1,4-Dichlorobenzene-d_4. The intermediate IS solution is prepared by diluting the stock solution(s) with methanol to a concentration of 100 µg/mL. The appropriate amount of IS solution is added to the water or soil sample or QC sample to achieve a final concentration of 100 ng/sample or standard. Internal standard is added at the same concentration to all standards, samples, and QC samples.

8.4.2 Surrogate Standard Solutions:

The surrogate standards are Dibromofluoromethane, 1,2-Dichloroethane-d_4, Toluene-d_8, and 4-Bromofluorobenzene. The intermediate surrogate solution is prepared by diluting the stock solution(s) with methanol to a concentration of 100 µg/mL. The appropriate amount of surrogate solution is added to the water or soil sample or QC sample to achieve a final concentration of 100 ng/sample.

8.4.3 Target Compound Solutions:

The target analytes routinely reported by this method are listed in the beginning of this SOP. The intermediate target compound solutions are prepared by diluting the stock solution(s) with methanol. This set of solutions, at concentrations of 200 µg/mL, is used for preparation of the calibration standards.

8.4.4 4-Bromofluorobenzene (BFB) Tune solution:

A solution containing BFB at a concentration of 50 µg/mL is prepared by volumetrically diluting the BFB stock solution. 1 µL of this solution is direct-injected or purged into the GC/MS system to verify system performance prior to any standard or sample analysis.

8.5 Calibration Standards:

There are two types of calibration standards used for this method – initial calibration standards and calibration verification standards.

8.5.1 Initial Calibration Standards:

Initial calibration standards can be prepared at the levels listed in Table 4 (other/different levels are allowed). The Initial Calibration needs to have a minimum of 5 standards, 6 if a quadratic curve fit is used. Prepare these solutions in organic-free reagent water. The standards correspond to the range of concentrations found in typical samples and do not exceed the working range of the GC/MS system. Initial calibration should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

8.5.2 Initial Calibration Verification Standard (ICV):

The initial calibration verification standard is at the same concentration as the level 3 initial calibration standard. This standard is made from a second source than the Initial Calibration Standards.

8.5.3 Continuing Calibration Verification Standard:

The continuing calibration verification standard, or calibration check standard, should be analyzed near the action level of the project. Since most projects are focused on achieving low reporting limits, the continuing calibration verification standard is at the same concentrations as the level 3 initial calibration standard. This standard is run at the beginning of each analytical sequence, following the BFB tune standard, to verify system performance.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

Blank samples must be matrix specific, i.e. methanol samples need to have methanol in the blank; sodium bisulfate samples need to have a sodium bisulfate blank analyzed; TCLP samples need a TCLP blank.

Analyze a matrix-specific blank each day prior to sample analysis to demonstrate that interferences from the analytical system are under control. The blank must contain the internal standards and surrogates.

Analyze the reagent water blank from the same source of water used for preparing the standards, QC samples and making sample dilutions. The method blank must not contain any target analytes at or above the compound reporting limits.

9.2 Laboratory Control Sample (LCS)/ Laboratory Control Sample Duplicate (LCSD)

A LCS/LCSD pair is analyzed at the beginning of each analytical sequence. Since the LCS contains the same compounds at the same concentrations as the continuing calibration check standard, the same analysis is used to satisfy both QC elements. The LCS/LCSD acceptance criteria are based on in-house control limits, unless specified by project/regulation.

9.3 Initial Calibration Verification (ICV)

Refer to Section 10.2.5.

9.4 Continuing Calibration Verification (CCV)

Refer to Section 10.4.4.

9.5 Matrix Spike/ Matrix Spike Duplicate

Upon Client Request, a matrix spike/matrix spike duplicate pair may be analyzed with each batch of 20 or less samples. The MS/MSD are sample aliquots spiked with the target compounds at the same concentration as the continuing calibration standard. The MS/MSD acceptance criteria are based on in-house control limits. If the MS/MSD does not meet the

criteria, but the LCSD does, the failure may be attributed to sample matrix. Report the MS/MSD, including a narrative sheet for inclusion with the client report.

9.6 Laboratory Duplicate

Not applicable.

9.7 Method-specific Quality Control Samples

9.7.1 Internal Standards

Area counts of the internal standard peaks in all samples and QC samples must be between 50-200% of the areas of the internal standards in the QC check standard.

If any individual percent recovery falls outside the range, that parameter has failed the acceptance criteria. For calibration standards, CCVs, LCS/LCSD or blanks the internal standard must be within the range for data to be reported to the clients. For samples, matrix spikes and duplicates: if the data is not within the range, the sample is rerun to confirm that the failure is due to sample matrix. A nonconformance report form is completed to ensure client notification and reporting if matrix effect is confirmed.

9.7.2 Surrogates

Surrogates are added to each field sample and QC sample. The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. The surrogate acceptance criteria are listed in Table 2. Since the SIM analysis is acquired in dual mode, the surrogates from the full scan are used to evaluate the entire sample (SIM and full scan).

9.8 Method Sequence

In a 12-hour period, the typical analytical sequence is as follows:

- BFB
- QC Check Standard/Laboratory Control Sample/LCSD
- Method Blank
- Samples
- MS/MSD (upon Client request, may be run anytime after the Method Blank)

10. Procedure

10.1 Equipment Set-up

Typical instrument operating conditions are listed below. Alternate conditions are allowed, as long as method performance criteria can be met.

10.1.1 GC Conditions:

Temperature 1:	35°C	Carrier gas:	Helium, 99.999%
Hold Time 1:	4 minutes	Carrier mode:	Constant flow
Ramp 1:	6°C/minute	Carrier flow:	1 mL/minute
Temperature 2:	150°C		
Hold Time 2:	0 minutes		
Ramp 2:	8°C/minute		
Temperature 3:	220°C		
Final Time:	1 minute		

10.1.2 MS Conditions:

Mass scan range: 35 – 260 amu
Scan time: 0.5 minutes/scan
Source temperature: 230°C

10.1.3 Velocity Concentrator Purge and Trap Conditions:

Purge time: 11 minutes
Dry purge: 2 minutes

Desorb preheat: 250°C
Desorb temp: 255°C
Desorb time: 2 minutes

Bake temp: 290°C
Bake time: 10 minutes

10.1.4 Encon Concentrator Purge and Trap Conditions:

Purge time: 11 minutes
Dry purge: 1 minute

Desorb preheat: 245°C
Desorb temp: 255°C
Desorb time: 1 minute

Bake temp: 270°C
Bake time: 10 minutes

10.2 Initial Calibration

10.2.1 The initial calibration is performed at a minimum of five (5) concentration levels listed in Table 4, the low level of the either at or below the reporting limit. The calibration is performed using instrument conditions listed in Section 10.1.

BFB must be analyzed prior to analysis of the initial calibration standards, and must pass the criteria listed in Table 3. The mass spectrum of BFB should be acquired in the following manner:

(1) Three scans (the peak apex scan, the scan immediately preceding the apex and the scan immediately following the apex) are acquired and averaged.
(2) Background subtraction is performed using a single scan of no more than 20 scans prior to the elution of BFB.

This is done automatically with the ThruPut Target / Enviroquant software.

10.2.1.1 Low Level/High Level Soil Curve on Archon or Centurion: To prepare a calibration standard, add the appropriate volume of standard solution(s) to a 50mL volumetric flask using a micro syringe. Remove the needle quickly and mix by inverting the flask 3 times. Pour several mLs of the aqueous standard into the waste vessel, then gently fill a 5mL syringe with standard and transfer to a 40mL VOA vial containing a magnetic stir bar. Load the vial onto autosampler.

10.2.1.2 Aqueous/High Level Soil Curve on Solatek or Centurion: To prepare a calibration standard, add the appropriate volume of standard solution(s) to a 100mL volumetric flask using a micro syringe. Remove the needle quickly and mix by inverting the flask 3 times. Pour several mLs of the aqueous standard into the waste vessel, then gently fill a 40mL VOA vial to the top. Load the vial onto the autosampler.

10.2.2 Establish the GC operating conditions by loading the appropriate GC method. Typical instrument conditions are listed in Section 10.1. The same operating conditions are used for calibration and sample analyses. Create the analytical sequence using the HP Enviroquant data acquisition software.

Relative Response Factors: The internal standard calibration technique is used. In each calibration standard, calculate the relative response factor for each analyte and the relative standard deviation (RSD) of the response factors using the Target / Enviroquant data processing software. The response factors are calculated using the areas of the characteristic (quantitation) ion for each target analyte and internal standard. The calculations are performed automatically using the Target / Enviroquant software, using the formulae listed in Alpha's Quality Manual.

10.2.3 Initial Calibration Criteria: The following sections outline the method acceptance criteria for an initial calibration curve. All criteria must be met for the calibration to be deemed acceptable, and for sample analysis to proceed.

10.2.3.1 Relative Standard Deviation Criteria: If the RSD for each target analyte is less than or equal to 20%, then the response for this compound is considered linear over the calibration range and the mean calibration factor can be used to quantitate sample results. If the 20% RSD criterion is not met for an analyte linear regression may be used if $\mathbf{r} \geq 0.990$, weighted linear with a weighting factor of 1/SD2 and $r > 0.990$, or quadratic fit if $\mathbf{r^2} \geq 0.995$. A minimum of six points is required and the low point of the calibration must be re-quantitated and recover within 70-130% to be deemed acceptable. The calibration must be repeated for any compounds that fail. If more than 10% of the compounds exceed the 20% RSD limit and do not achieve the minimum correlation coefficient for alternative curve fits, sample analysis cannot proceed.

10.2.3.2 Minimum Response Factors: Table 1 lists the suggested minimum response factors for the most common analytes. Each calibration level must be evaluated against the specified criteria. Analytes that fall below the criteria, but are greater than or equal to 0.05, are narrated for inclusion on the final report. There are certain very poor purgers (1,4-Dioxane, Acrolein, ketones, alcohols and other water soluble compounds) that should meet a 0.001 response factor. If an analyte falls below 0.05 (or 0.001 for 1,4-Dioxane, Acrolein, ketones, alcohols and other water soluble compounds), then corrective action must be taken to resolve the problem before analysis can proceed.

10.2.4 Evaluation of Retention Times: The relative retention times used for identification of target analytes are +/- 0.06 RRT (Relative Retention Time) units, based on the most recent standard run. It has been determined that these limits work well, being wide enough to eliminate false-negative results while being tight enough to eliminate false positive results. Due to the selectivity of the mass spectrometer, compound identification is more definitive than when using a less selective detector.

10.2.5 Initial Calibration Verification: After each calibration and before the analysis of samples, an ICV must be analyzed at or near the midpoint of the curve. The ICV must be prepared using a different source than the Initial Calibration and must contain all target analytes. The percent recoveries must be between 70% and 130% for target analytes except for "difficult" analytes (Table 7), which must exhibit percent recoveries between 40% and 160%. Corrective action is required if greater than 10% of all analytes are outside the prescribed criteria.

10.3 Equipment Operation and Sample Processing

The same GC, MS, and Purge and Trap conditions used for the initial calibration must be employed for sample analysis. After verification of system performance by analysis of BFB, the continuing calibration standard and method blank, samples are analyzed and processed as described below.

10.3.1 Analysis of Samples

Retrieve sample VOA vials from the sample bank refrigerator just prior to loading onto the purge and trap system. High level soil samples must be shaken for 1 – 2 minutes to extract the volatile components into the methanol. Let sample settle prior to taking methanol aliquot. Low level soil sample should be shaken briefly to ensure that the stir bar is loose, and will spin on the Archon or Centurion unit.

10.3.1.1 Low level soil samples: (Archon or Centurion)

Take the low level VOA vial and place directly into the rack of the Archon sampling unit. Surrogate and internal standards are added automatically by the Archon prior to sample purging.

10.3.1.2 Aqueous samples: (Solatek or Centurion)

Load the VOA vial directly on the sampling rack. Dilutions may be prepared volumetrically and poured into VOA vials ensuring there is no headspace left in the vial. The auto-sampler will then sample 10mL from the VOA vial.

10.3.1.3 High level soil samples: (Archon/Solatek/Centurion)

Shake for 2 minutes, ensuring the methanol has completely penetrated the soil in the vial.

10.3.1.3.1 Through liquid path

Load a maximum of 430µL or appropriate dilution of the methanol into a half-full VOA vial. Fill the VOA vial up to the top with water and cap with no headspace. Allow the auto-sampler to sample 10mL out of the VOA vial which would be equivalent to injecting 100µL of the methanol extract. Prepare dilutions accordingly.

10.3.1.3.2 Through soil path

Into a VOA vial with a stir bar added, load 4.9mL of water plus a maximum of 100 µL of methanol or appropriate dilution of methanol extract from a 5mL luerlock syringe. Cap the vial and load onto the auto-sampler.

10.3.2 Qualitative Analysis:

10.3.2.1 The qualitative identification of each compound is based on retention time and on comparison of the sample mass spectrum with the reference mass spectrum. The reference mass spectrum must be generated by the laboratory on the same

GC/MS system. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met:

10.3.2.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. The Target / Enviroquant data system is configured to make this check.

10.3.2.1.2 The relative retention time (RRT) of the sample component is within ±0.06 RRT units of the RRT of the standard component.

10.3.2.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

10.3.2.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs (i.e., m and p-xylene).

10.3.2.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

10.3.2.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

10.3.2.2 For samples containing non-target analytes, a library search will be performed at client request. Compound identification will be classified as “tentative”, and the concentration will be reported as an estimate as no quantitative standards are run for these compounds.

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.
2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)
3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

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 coeluting peaks.

10.3.3 Quantitative Analysis:

10.3.3.1 Quantitation of a target compound detected in a sample is performed automatically by the Target / Enviroquant data processing software, using the formulae found in Alpha's Quality Manual. Either the average response factor or calibration curve will be used for sample quantitation, depending on how the particular analyte was processed in the initial calibration curve.

If non-target compounds are to be reported, the quantitation is performed automatically by the Target / Enviroquant software using the total area of the compound and the nearest internal standard, and assuming a relative response factor of 1.0.

10.4 Continuing Calibration

Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

10.4.1 Prior to the analysis of samples or calibration standards, inject or purge 1 µL (50 ng) of the 4-Bromofluorobenzene standard (Section 8.4.4) into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 3 before sample analysis begins.

10.4.2 The initial calibration curve for each compound of interest must be verified once every 12 hours prior to sample analysis. This is accomplished by analyzing the continuing calibration check standard (Section 8.5.3).

10.4.3 A method blank must be analyzed prior to any samples, typically immediately following the continuing calibration check standard, to ensure that the analytical system is free of contaminants. The method blank must not contain any target analytes at or above the required compound reporting limits.

10.4.4 The percent difference or drift for each target analyte must be less than or equal to 20% (30% for all SIM compounds). If greater than 20% of target analytes exceed the %D criteria corrective action must be taken prior to the analysis of samples. If less than or equal to 20% of compounds exceed the criteria, corrective action is not required.

10.4.5 The continuing calibration standard must also be evaluated for the suggested minimum response factor criteria, as specified in section 10.2.3.2

10.4.6 Internal Standard Retention Time:

The retention times of the internal standards in the calibration verification standard are evaluated after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for

malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

10.4.7 Internal Standard Response:

If the area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is required.

10.5 Preventive Maintenance

Routine preventive maintenance should be performed on the analytical system. This includes replacement of GC septa and periodic rinsing or replacement of purge and trap tubes and sparge needles. The trap should be replaced every six months, or sooner if performance criteria cannot be met. Periodic cleaning (typically twice per year) of the mass spectrometer ion source is required. More frequent source cleaning may be needed, especially if dirty samples are analyzed.

If system performance deteriorates, additional maintenance may be required. This includes replacement of injector ports and seals, clipping several inches off of the front end of the GC column, or in extreme cases the replacement of the GC column. Flushing or replacement of purge and trap lines may be necessary if they become contaminated or develop active sites.

Perform routine preventative maintenance as described throughout this SOP. Record all maintenance in the instrument logbook.

11. Data Evaluation, Calculations and Reporting

11.1.1 LIMS Data Corrections

Please note that the Laboratory Information Management System (LIMS) automatically adjusts soil sample results to account for the % Total Solids of the sample (as determined per Alpha SOP/07-38) and the methanol preservation dilution effect.

11.1.2 Data Calculations

11.1.2.1 Results of Aqueous Sample Analysis:

$$Concentration\ (ug/L) = \frac{(Conc.)\ (Vp)\ (DF)}{(Vs)}$$

where:

Conc. = On-column concentration obtained from the quantitation report.
Vp = Volume purged, 10 mL is standard
Vs = Volume of sample purged
DF = Dilution factor, for manually prepared dilutions, not instrumental "dilutions".

11.1.2.2 Results of Sediment/Soil, Sludge, and Waste Analysis: All solids including soils, sediments, and sludges must be reported on a dry-weight basis.

11.1.2.2.1 Low-Level Samples:

$$Concentration\ (ug/Kg) = \frac{(Conc.)\ (Vp)\ (DF)}{(W)\ (\%S)}$$

11.1.2.2.2 High-Level Samples:

$$Concentration\ (ug/Kg) = \frac{(Conc.)\ (Vp)\ (5000)\ (DF)}{(W)\ (Ve)\ (\%S)}$$

where:

Conc. = On-column concentration obtained from the quantitation report.
DF = Dilution factor, for manually prepared dilutions, not instrumental "dilutions".
Ve = Extract volume, mL
Vp = Volume purged, 5 mL is standard
W = Aliquot of sample (wet), g
%S = Sample % solid
5000 = Constant representing the final volume of the methanol extraction.

11.1.2.2.3 High-Level Samples Corrected for Total Water/Solvent Mixture (V_t):

Samples that are extracted prior to analysis in a water miscible solvent such as methanol are diluted by the total volume of the water/solvent mixture. The total mixture volume can only be calculated based on the sample moisture present as determined by the % moisture calculation.

$$\%\ moisture = \frac{g\ of\ sample - g\ of\ dry\ sample}{g\ of\ sample} \times 100$$

$$V_t = \frac{[mL\ of\ solvent + (\%moisture \times g\ of\ sample)]}{100} \times 1000mL/mL$$

The calculated V_t value is now added to the volume of methanol in the sample (typically 5000µL), and the corrected concentration is calculated using the equation below:

$$Corrected\ concentration\ (mg/Kg) = \frac{(Conc.)\ (V_t + methanol\ vol.)\ (Vp)\ (DF)}{(W)\ (Ve)\ (\%S)}$$

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

All batch and sample specific QC criteria outlined in section 10 are evaluated by the analyst prior to approval of the data. When any QC criteria fail, the cause for the failure must be identified and corrected. This may include instrument recalibration followed by sample reanalysis, sample cleanup, or sample re-extraction. If it is determined that the failure is due to sample matrix effects, a project narrative report is written by the analyst for inclusion in the data report. If there is insufficient sample volume to perform the re-analysis for confirmation, this is also noted in the narrative and included in the client report.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

SOP/14-01 Waste Management and Disposal SOP

16. Attachments

TABLE 1: 8260 REPORTING LIMITS

TABLE 2: 8260 QC ACCEPTANCE CRITERIA

TABLE 3: BFB TUNING CRITERIA

TABLE 4: STANDARD SOLUTIONS

TABLE 5: 8260C Volatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

TABLE 6: 8260C Quantitation Ions

Table 1
Standard Reported Detection Limits
US EPA METHOD 8260C and 5035A/8260C

Analyte	Recommended Minimum Response Factor	RDL (µg/L)	RDL(µg/KG)[1]	RDL (µg/KG)[2]
Acetone [3,4,5]	0.100	5.0	10	250
Acrolein [5]		5.0	25	1250
Acrylonitrile [3,4]		5.0	5	200
Benzene [3,4,5]	0.500	0.5	1	50
Bromobenzene [3,4]		2.5	5	250
Bromochloromethane [3,4,5]		2.5	5	250
Bromodichloromethane [3,4,5]	0.200	0.5	1	50
Bromoform [3,4,5]	0.100	2.0	4	200
Bromomethane [3,4,5]	0.100	1.0	2	100
2-Butanone [3,4,5]	0.100	5.0	10	500
n-Butyl benzene [3,4]		0.5	1	50
sec-Butyl benzene [3,4]		0.5	1	50
tert-Butyl benzene [3,4]		2.5	5	250
Carbon disulfide [3,4,5]	0.100	5.0	10	500
Carbon tetrachloride [3,4,5]	0.100	0.5	1	50
Chlorobenzene [3,4,5]		0.5	1	50
Chloroethane [3,4,5]	0.100	1.0	2	100
2-Chloroethylvinyl ether [3]		10.0	20	1000
Chloroform [3,4,5]	0.200	0.75	1.5	75
Chloromethane [3,4,5]	0.100	2.5	5	250
o-Chlorotoluene [3,4]		2.5	5	250
Cyclohexane [5]	0.100	10	20	1000
Cyclohexanone		10	20	1000
p-Chlorotoluene [3,4]		2.5	5	250
Dibromochloromethane [3,4,5]	0.100	0.5	1	50
1,2-Dibromo-3-chloropropane [3,4,5]	0.050	2.5	5	250
1,2-Dibromoethane [3,4,5]	0.100	2.0	5	250
Dibromomethane [3,4]		5.0	10	500
1,2-Dichlorobenzene [3,4,5]	0.400	2.5	5	250
1,3-Dichlorobenzene [3,4,5]	0.600	2.5	5	250
1,4-Dichlorobenzene [3,4,5]	0.500	2.5	5	250
1,4-Dichlorobutane [3,4]		5.0	10	500
trans-1,4-Dichloro-2-butene [3,4]		2.5	5	250
Dichlorodifluoromethane [3,4,5]		5.0	10	500
1,1-Dichloroethane [3,4,5]	0.200	0.75	1.5	75
1,2-Dichloroethane [3,4,5]	0.100	0.5	1	50
1,1-Dichloroethene [3,4,5]	0.100	0. 5	1	50
cis-1,2-Dichloroethene [3,4,5]	0.100	0.5	1	50
trans-1,2-Dichloroethene [3,4,5]	0.100	0.75	1.5	75

Table 1 (continued)

Standard Reported Detection Limits

US EPA METHOD 8260C and 5035A/8260C

Analyte	Recommended Minimum Response Factor	RDL (µg/L)	RDL(µg/KG)[1]	RDL (µg/KG)[2]
1,2-Dichloropropane [3,4,5]	0.100	1.75	3.5	175
1,3-Dichloropropane [3,4]		2.5	5	250
2,2-Dichloropropane [3,4]		2.5	5	250
1,1-Dichloropropene [3,4]		2.5	2.5	250
cis-1,3-Dichloropropene [3,4,5]	0.200	0.5	1	50
p-Diethylbenzene [4]		2.0	4	200
Diisopropyl Ether [6]		2.0	4	200
1,4-Dioxane [5] (non-SIM)		250	100	5000
trans-1,3-Dichloropropene [3,4,5]	0.200	0.5	1	50
Ethanol [7]		N/A	1000	50000
Ethyl acetate		10.0	20	1000
Ethylbenzene [3,4,5]	0.100	0.5	1	50
Ethyl ether [3,4]		2.5	5	250
4-Ethyltoluene [4]		2.0	4	200
Ethyl methacrylate [3,4]		5.0	10	500
Ethyl-Tert-Butyl-Ether [6]		2.0	4	200
Freon-113 [5]		10.0	20	1000
Hexachlorobutadiene [3,4]		0.5	5	250
Hexane		1.0	1.0	50
2-Hexanone [3,4,5]	0.100	5.0	10	500
Iodomethane		5.0		
Isopropyl Alcohol (IPA)		25		
Isopropylbenzene [3,4,5]	0.100	0.5	1	50
p-Isopropyltoluene [3,4]		0.5	1	50
Methyl Acetate [5]	0.100	20	20	1000
Methylene chloride [3,4,5]	0.100	3.0	10	500
Methyl Cyclohexane [5]	0.100	20	4	200
Methyl Methacrylate		1.0		
4-Methyl-2-pentanone [3,4,5]	0.100	5.0	10	500
Methyl-tert-butyl-ether [3,4,5]	0.100	1.0	2	100
Naphthalene [3,4]		2.5	5	250
n-Butanol [5]		100	200	10000
n-Propylbenzene [3,4]		0.5	1	50
n-Propyl bromide		5.0		
Pentachloroethane		2.0	N/A	N/A
Styrene [3,4,5]	0.300	1.0	2	100
Tert-Butyl Alcohol [5]		30	100	5000
Tertiary-Amyl Methyl Ether [6]		2.0	4	200

Analyte	Recommended Minimum Response Factor	RDL (µg/L)	RDL(µg/K (1)	RDL(µg/K (2)
1,1,1,2-Tetrachloroethane (3,4)		0.5	1	50
1,2,4,5-Tetramethylbenzene (4)		2.0	4	200
1,1,2,2-Tetrachloroethane (3,4,5)	0.300	0.5	1	50
Tetrachloroethene (3,4,5)	0.200	0.5	1	50
Tetrahydrofuran (3)		10.0	20	1000
Toluene (3,4,5)	0.400	0.75	1	75
1,2,3-Trichlorobenzene (3,4,5)		2.5	5	250
1,2,4-Trichlorobenzene (3,4,5)	0.200	2.5	5	250
1,3,5-Trichlorobenzene (6)		2.0	5	250
1,1,1-Trichloroethane (3,4,5)	0.100	0.5	1	50
1,1,2-Trichloroethane (3,4,5)	0.100	0.75	1.5	75
Trichloroethene (3,4,5)	0.200	0.5	1	50
Trichlorofluoromethane (3,4,5)	0.100	2.5	5	250
1,2,3-Trichloropropane (3,4)		5.0	10	500
1,2,4-Trimethylbenzene (3,4)		2.5	5	250
1,3,5-Trimethylbenzene (3,4)		2.5	5	250
Vinyl acetate (3,4)		5.0	10	500
Vinyl chloride (3,4,5)	0.100	1.0	2	100
m/p-Xylenes (3,4,5)	0.100	1.0	2	100
o-Xylene (3,4,5)	0.300	1.0	2	100
1,4-Dioxane (5) SIM		3.0		
1,1,2,2-Tetrachloroethane SIM		0.1		

(1) Detection Limits are for Low-level Aqueous preserved samples.
(2) Detection Limits are for High-level Methanol preserved samples.
(3) Analyte reported by standard 8260 reporting list.
(4) Analyte reported by New York TCL reporting list.
(5) Analyte reported by New Jersey TCL reporting list.
(6) Analyte reported for New Hampshire in addition to standard 8260 reporting list.
(7) Analyte only reported for New York TCL report upon client request.

Note: Reporting Limits are based on standard 8260 reporting list, RL's may vary for New York and New Jersey reporting lists.

Table 2

QUALITY CONTROL ACCEPTANCE CRITERIA

Surrogate Spike Percent Recovery	Aqueous Limits		Soil Limits	
	Lower Control Limit	Upper Control Limit	Lower Control Limit	Upper Control Limit
1,2-Dichloroethane-d_4	70%	130%	70%	130%
4-Bromofluorobenzene	70%	130%	70%	130%
Toluene-d_8	70%	130%	70%	130%
Dibromofluoromethane	70%	130%	70%	130%

Table 3

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

Table 4

Stock Standard Concentrations and Suggested Calibration Concentration Levels

Target Compound	Stock (µg/mL)	Level 1 (µg/L)	Level 2 (µg/L)	Level 3 (µg/L)	Level 4 (µg/L)	Level 5 (µg/L)	Level 6 (µg/L)	Level 7 (µg/L)	Level 8 (µg/L)
Acetone	2000	0.5	2	10	20	30	50	100	200
Acrolein	2000	0.5	2	10	20	30	50	100	200
Acrylonitrile	2000	0.5	2	10	20	30	50	100	200
Benzene	2000	0.5	2	10	20	30	50	100	200
Bromobenzene	2000	0.5	2	10	20	30	50	100	200
Bromochloromethane	2000	0.5	2	10	20	30	50	100	200
Bromodichloromethane	2000	0.5	2	10	20	30	50	100	200
Bromoform	2000	0.5	2	10	20	30	50	100	200
Bromomethane	2000	0.5	2	10	20	30	50	100	200
2-Butanone	2000	0.5	2	10	20	30	50	100	200
n-Butyl benzene	2000	0.5	2	10	20	30	50	100	200
sec-Butyl benzene	2000	0.5	2	10	20	30	50	100	200
tert-Butyl benzene	2000	0.5	2	10	20	30	50	100	200
Carbon disulfide	2000	0.5	2	10	20	30	50	100	200
Carbon tetrachloride	2000	0.5	2	10	20	30	50	100	200
Chlorobenzene	2000	0.5	2	10	20	30	50	100	200
Chloroethane	2000	0.5	2	10	20	30	50	100	200
2-Chloroethylvinyl Ether	2000	0.5	2	10	20	30	50	100	200
Chloroform	2000	0.5	2	10	20	30	50	100	200
Chloromethane	2000	0.5	2	10	20	30	50	100	200
o-Chlorotoluene	2000	0.5	2	10	20	30	50	100	200
p-Chlorotoluene	2000	0.5	2	10	20	30	50	100	200
Cyclohexane	2000	0.5	2	10	20	30	50	100	200
Cyclohexanone	2000	0.5	2	10	20	30	50	100	200
Dibromochloromethane	2000	0.5	2	10	20	30	50	100	200
1,2-Dibromo-3-chloropropane	2000	0.5	2	10	20	30	50	100	200
1,2-Dibromoethane	2000	0.5	2	10	20	30	50	100	200
Dibromomethane	2000	0.5	2	10	20	30	50	100	200
1,2-Dichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,3-Dichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,4-Dichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,4-Dichlorobutane	2000	0.5	2	10	20	30	50	100	200
trans-1,4-Dichloro-2-butene	2000	0.5	2	10	20	30	50	100	200
Dichlorodifluoromethane	2000	0.5	2	10	20	30	50	100	200
1,1-Dichloroethane	2000	0.5	2	10	20	30	50	100	200
1,2-Dichloroethane	2000	0.5	2	10	20	30	50	100	200
1,1-Dichloroethene	2000	0.5	2	10	20	30	50	100	200
cis-1,2-Dichloroethene	2000	0.5	2	10	20	30	50	100	200
trans-1,2-Dichloroethene	2000	0.5	2	10	20	30	50	100	200
1,2-Dichloropropane	2000	0.5	2	10	20	30	50	100	200
1,3-Dichloropropane	2000	0.5	2	10	20	30	50	100	200
2,2-Dichloropropane	2000	0.5	2	10	20	30	50	100	200
1,1-Dichloropropene	2000	0.5	2	10	20	30	50	100	200

Table 4 (continued)

Stock Standard Concentrations and Suggested Calibration Concentration Levels

Target Compound	Stock (µg/mL)	Level 1 (µg/L)	Level 2 (µg/L)	Level 3 (µg/L)	Level 4 (µg/L)	Level 5 (µg/L)	Level 6 (µg/L)	Level 7 (µg/L)	Level 8 (µg/L)
cis-1,3-Dichloropropene	2000	0.5	2	10	20	30	50	100	200
trans-1,3-Dichloropropene	2000	0.5	2	10	20	30	50	100	200
p-Diethylbenzene	2000	0.5	2	10	20	30	50	100	200
Diisopropyl Ether	2000	0.5	2	10	20	30	50	100	200
1,4-Dioxane (non-SIM)	10000	100	400	1000	2000	3000	4000	5000	6000
Ethanol	10000	100	200	300	500	1000	2500	5000	N/A
Ethyl Acetate	2000	0.5	2	10	20	30	50	100	200
Ethylbenzene	2000	0.5	2	10	20	30	50	100	200
Ethyl ether	2000	0.5	2	10	20	30	50	100	200
Ethyl methacrylate	2000	0.5	2	10	20	30	50	100	200
Ethyl Tert-Butyl Ether	2000	0.5	2	10	20	30	50	100	200
4-Ethyltoluene	2000	0.5	2	10	20	30	50	100	200
Freon-113	2000	0.5	2	10	20	30	50	100	200
Halothane	2000	0.5	2	10	20	30	50	100	200
Hexachlorobutadiene	2000	0.5	2	10	20	30	50	100	200
2-Hexanone	2000	0.5	2	10	20	30	50	100	200
Hexane	2000	0.5	2	10	20	30	50	100	200
Iodomethane	2000	0.5	2	10	20	30	50	100	200
Isopropyl Alcohol (IPA)	10000	2.5	10	50	100	150	250	500	1000
Isopropylbenzene	2000	0.5	2	10	20	30	50	100	200
p-Isopropyltoluene	2000	0.5	2	10	20	30	50	100	200
Methyl Acetate	2000	0.5	2	10	20	30	50	100	200
Methylene Chloride	2000	0.5	2	10	20	30	50	100	200
Methyl Cyclohexane	2000	0.5	2	10	20	30	50	100	200
Methyl Methacrylate	2000	0.5	2	10	20	30	50	100	200
4-Methyl-2-pentanone	2000	0.5	2	10	20	30	50	100	200
Methyl-tert-butyl-ether	2000	0.5	2	10	20	30	50	100	200
Naphthalene	2000	0.5	2	10	20	30	50	100	200
n-Butanol	5000	2.5	10	50	100	150	250	500	N/A
n-Propylbenzene	2000	0.5	2	10	20	30	50	100	200
n-Propyl bromide	2000	0.5	2	10	20	30	50	100	200
Pentachloroethane	1000	0.5	2	10	20	30	50	100	200
Styrene	4000	1	4	20	40	60	100	200	400
Tert-Butyl alcohol	10000	2.5	10	50	100	150	250	500	1000
Tertiary-Amyl Methyl Ether	2000	0.5	2	10	20	30	50	100	200
1,1,1,2-Tetrachloroethane	2000	0.5	2	10	20	30	50	100	200
1,1,2,2-Tetrachloroethane	2000	0.5	2	10	20	30	50	100	200
Tetrachloroethene	2000	0.5	2	10	20	30	50	100	200
Tetrahydrofuran	2000	0.5	2	10	20	30	50	100	200
1,2,4,5-Tetramethylbenzene	2000	0.5	2	10	20	30	50	100	200
Toluene	2000	0.5	2	10	20	30	50	100	200
1,2,3-Trichlorobenzene	2000	0.5	2	10	20	30	50	100	200

Table 4 (continued)

Stock Standard Concentrations and Suggested Calibration Concentration Levels

Target Compound	Stock (µg/mL)	Level 1 (µg/L)	Level 2 (µg/L)	Level 3 (µg/L)	Level 4 (µg/L)	Level 5 (µg/L)	Level 6 (µg/L)	Level 7 (µg/L)	Level 8 (µg/L)
1,2,4-Trichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,3,5-Trichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,1,1-Trichloroethane	2000	0.5	2	10	20	30	50	100	200
1,1,2-Trichloroethane	2000	0.5	2	10	20	30	50	100	200
Trichloroethene	2000	0.5	2	10	20	30	50	100	200
Trichlorofluoromethane	2000	0.5	2	10	20	30	50	100	200
1,2,3-Trichloropropane	2000	0.5	2	10	20	30	50	100	200
1,2,4-Trimethylbenzene	2000	0.5	2	10	20	30	50	100	200
1,3,5-Trimethylbenzene	2000	0.5	2	10	20	30	50	100	200
Vinyl acetate	2000	0.5	2	10	20	30	50	100	200
Vinyl chloride	2000	0.5	2	10	20	30	50	100	200
m/p-Xylenes	4000	1	4	20	40	60	100	200	400
o-Xylene	4000	1	4	20	40	60	100	200	400
1,4-Dioxane (SIM)	100	0.5	2	10	20	30	50	100	200
1,1,2,2-Tetrachloroethane (SIM)		0.05	0.1	0.2	0.5	1.0	2.0	5.0	10.0

Target Compounds	Stock (µg/mL)	Level 1 (µg/L)	Level 2 (µg/L)	Level 3 (µg/L)	Level 4 (µg/L)	Level 5 (µg/L)	Level 6 (µg/L)	Level 7 (µg/L)	Level 8 (µg/L)
Internal Standards									
Fluorobenzene	2500	10	10	10	10	10	10	10	10
Chlorobenzene-d5	2500	10	10	10	10	10	10	10	10
1,4-Dichlorobenzene-d4	2500	10	10	10	10	10	10	10	10
Surrogates									
Dibromofluoromethane	2500	10	10	10	10	10	10	10	10
1,2-Dichloroethane-d4	2500	10	10	10	10	10	10	10	10
Toluene-d8	2500	10	10	10	10	10	10	10	10
4-Bromofluorobenzene	2500	10	10	10	10	10	10	10	10

- For Low Level Soil analysis, the calibration levels are the same in µg/Kg units.
- For High Level Soil analysis, the calibration levels are at 50x the levels listed due to sample preparation requirements.

TABLE 5

8260C Volatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

Fluorobenzene	Chlorobenzene-d5	1,4-Dichlorobenzene-d4
Dichlorodifluoromethane	Toluene-d8 (surr)	Isopropylbenzene
Chloromethane	Toluene	Bromoform
Vinyl Chloride	Ethyl Methacrylate	1,4-dichloro-2-butane
Bromomethane	Trans-1,3-dichloropropene	1,1,2,2,-tetrachloroethane
Chloroethane	1,1,2-trichloroethane	4-bromofluorobenzene (surr)
Trichlorofluoromethane	2-hexanone	1,2,3-trichloropropane
Ethyl Ether	1,3-dichloropropane	trans-1,4-dichloro-2-butene
Freon 113	Tetrachloroethene	n-propylbenzene
Acrolein	Chlorodibromomethane	Bromobenzene
Acetone	1,2-dibromoethane	4-ethyltoluene
Ethanol	Chlorobenzene	1,3,5-trimethybenzene
1,1,-dichloroethene	1,1,1,2-tetrachloroethane	2-chlorotoluene
Tert-Butyl Alcohol	Ethylbenzene	4-chorotoluene
Methyl Acetate	p/m xylene	tert-butylbenzene
Carbon Disulfide	o xylene	1,2,4-trimethylbenzene
Methylene Chloride	Styrene	sec-butylbenzene
Acrylonitrile		p-isopropyltoluene
Methyl Tert Butyl Ether		1,3-dichlorobenzene
Halothane		1,4-dichlorobenzene
Trans-1,2-dichloroethene		n-butylbenzene
Diisopropyl Ether		p-diethylbenzene
Vinyl Acetate		1,2-dichlorobenzene
1,1-dichloroethane		1,2,4,5-tetramethylbenzene
Ethyl-Tert-Butyl-Ether		1,2-dibromo-3-chloropropane
2-butanone		1,3,5-trichlorobenzene
2,2-dichloropropane		1,2,4-trichlorobenzene
Cis-1,2-dichloroethene		Hexachlorobutadiene
Chloroform		Naphthalene
Bromochloromethane		1,2,3-trichlorobenzene
Tetrahydrofuran		Cyclohexanone
Dibromofluoromethane (surr)		1,3,5-Trichlorobenzene
1,1,1-trichloroethane		Pentachloroethane
Cyclohexane		
1,1-dichloropropene		
Carbon Tetrachloride		
Tertiary-Amyl Methyl Ether		
1,2-dichloroethane-d4 (surr)		
1,2-dichloroethane		
Benzene		
Trichloroethene		
Methyl Cyclohexane		
1,2-dichloropropane		
Bromodichloromethane		
1,4-Dioxane		
Dibromomethane		
2-Chloroethylvinyl Ether		
4-methyl-2-pentanone		
Cis-1,3-dichloropropene		
Iodomethane		
Methyl methacrylate		
n-Butanol		
Ethyl acetate		
Isopropyl Alcohol (IPA)		
Hexane		
n-Propyl bromide		

TABLE 6
8260C Quantitation Ions

Analyte	Quantitation Ion	Analyte	Quantitation Ion
Dichlorodifluoromethane	85	Ethyl Methacrylate	69
Chloromethane	50	Trans-1,3-dichloropropene	75
Vinyl Chloride	62	1,1,2-trichloroethane	83
Bromomethane	94	2-hexanone	43
Chloroethane	64	1,3-dichloropropane	76
Trichlorofluoromethane	101	Tetrachloroethene	166
Ethyl Ether	74	Chlorodibromomethane	129
Freon 113	101	1,2-dibromoethane	107
Acrolein	56	Chlorobenzene	112
Acetone	43	1,1,1,2-tetrachloroethane	131
1,1,-dichloroethene	96	Ethylbenzene	91
Tert-Butyl Alcohol	59	p/m xylene	106
Methyl Acetate	43	o xylene	106
Carbon Disulfide	84	Styrene	104
Methylene Chloride	76	Isopropylbenzene	105
Acrylonitrile	53	Bromoform	173
Methyl Tert Butyl Ether	73	1,4-dichloro-2-butane	55
Halothane	117	1,1,2,2,-tetrachloroethane	83
Trans-1,2-dichloroethene	96	1,2,3-trichloropropane	75
Diisopropyl Ether	45	Trans-1,4-dichloro-2-butene	53
Vinyl Acetate	43	n-propylbenzene	91
1,1-dichloroethane	63	Bromobenzene	156
Ethyl-Tert-Butyl-Ether	59	4-ethyltoluene	105
2-butanone	43	1,3,5-trimethybenzene	105
2,2-dichloropropane	77	2-chlorotoluene	91
Cis-1,2-dichloroethene	96	4-chorotoluene	91
Chloroform	83	tert-butylbenzene	119
Bromochloromethane	128	1,2,4-trimethylbenzene	105
Tetrahydrofuran	42	sec-butylbenzene	105
1,1,1-trichloroethane	97	p-isopropyltoluene	119
Cyclohexane	56	1,3-dichlorobenzene	146
1,1-dichloropropene	75	1,4-dichlorobenzene	146
Carbon Tetrachloride	117	n-butylbenzene	91
Tertiary-Amyl Methyl Ether	73	p-diethylbenzene	119
1,2-dichloroethane	62	1,2-dichlorobenzene	146
Benzene	78	1,2,4,5-tetramethylbenzene	119
Trichloroethene	95	1,2-dibromo-3-chloropropane	75
Methyl Cyclohexane	83	1,3,5-trichlorobenzene	180
1,2-dichloropropane	63	1,2,4-trichlorobenzene	180
Bromodichloromethane	83	Hexachlorobutadiene	225
1,4-dioxane	88	Naphthalene	128
Dibromomethane	93	1,2,3-trichlorobenzene	180
2-Chloroethylvinyl Ether	63	Ethanol	45
4-methyl-2-pentanone	58	Cyclohexanone	55
Cis-1,3-dichloropropene	75	Ethyl acetate	43

TABLE 6
8260C Quantitation Ions (continued)

Analyte	Quantitation Ion	Analyte	Quantitation Ion
Toluene	92	Iodomethane	142
Methyl methacrylate	69	n-Butanol	56
Pentachloroethane	167	Isopropyl Alcohol (IPA)	45
Hexane	57	n-Propyl bromide	43

Table 7

List of 8260 Difficult Analytes:

1,1,2,2-Tetrachloroethane
1,2-Dibromo-3-chloropropane (DBCP)
1,4-Dioxane
2-Butanone
2-chloroethylvinyl ether
2-Hexanone
2,2-dichloropropane
4-Methyl-2-pentanone
Acetone
Bromoform
Bromomethane
Carbon disulfide
Chloroethane
Chloromethane
cis-1,3-Dichloropropene
Dichlorodifluoromethane (Freon 12)
Ethanol
Iodomethane
Isobutyl Alcohol
Naphthalene
n-butanol
Styrene
Tert-Butyl Alcohol
Trichlorofluoromethane (Freon 11)
Isopropyl Alcohol (IPA)

Appendix D: References

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