Soil Vapor Investigation Work Plan

Phillips 66/Former Tidewater Site
2800 Martin Luther King Jr Way South
Seattle, Washington

GHD | 732 Broadway, Suite 301, Tacoma, WA 98402

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1. Introduction

On December 8, 2016 the Washington State Department of Ecology (Ecology) and Mount Baker Housing Association (MBHA) entered into a prospective purchaser consent decree (the PPCD) for several adjacent properties in south Seattle, two of which had been previously listed on Ecology's Hazardous Sites List (the Mount Baker Cleaners site and the Phillips 66 070644 Site). Under the PPCD, all of the properties were collectively designated as the Mount Baker Properties Site (the Site). The PPCD, among other things, requires MBHA to perform a remedial investigation (RI) for the Site that defines the nature and extent of hazardous contamination. MBHA's work on the RI is ongoing. GHD is submitting this Soil Vapor Investigation Work Plan on behalf of Phillips 66 Company (P66) and Chevron Environmental Management Company (CEMC) and in cooperation with MBHA for one of the properties that makes up the Site. The property being investigated is the former Tidewater service station located at 2800 Martin Luther King Jr. Way South, Seattle, King County, Washington previously known as the Phillips 66 070644 Site (Property; Figure 1). This Work Plan is being submitted because the Site includes chlorinated solvents releases from a former dry cleaner located upgradient from the Property. The purpose of the soil vapor investigation described below is to determine whether the soil vapor intrusion pathway is complete for petroleum and chlorinated solvent impacts and determine whether there is an on-property source of chlorinated solvents. The results of the soil vapor investigation will be submitted to Ecology as a technical memo and provided to MBHA for inclusion in their Remedial Investigation (RI) Report.

1.1 Property Description and Background

The Property is a former Tidewater service station located on the southeast intersection of Martin Luther King Jr. Way South and South McClellan Street. The Property's location within the Site is shown on Figure 2. The Property is currently a vacant lot with the former service station building present. The last known use of the building was an auto detailing facility.

Prior to entry of the PPCD, the Property was enrolled in Ecology's Voluntary Cleanup Program (VCP) and, starting in 2005, was the subject of several remedial actions by P66 and CEMC to characterize and remediate petroleum contamination, including investigating the nature and extent of contamination, the removal of underground storage tanks and other equipment, and the excavation and off-site disposal of petroleum contaminated soil.

Over the past year MBHA has undertaken further investigation at the Property as part of the larger RI activities for the Site required by the PPCD. MBHA's activities at the Property have included Installation of four additional monitoring wells (AMW-04, AMW-05, AMW-12, and AMW-13), three soil borings (AB-23, AB-25, and ADP-24), and two sub-slab soil vapor probes (ASV-06 and ASV-07) to further investigate impacts from the petroleum release at the Property and the chlorinated solvents release from the up-gradient dry cleaner.

1.1.1 Upgradient Chlorinated Solvent Cleanup

A dry cleaner located northeast and up-gradient of the Property has operated since the 1940's until February 2017. The dry cleaner property, prior to entry of the Site under the PPCD, was known as

the Mount Baker Cleaners site. Investigations completed prior to entry of the PPCD, as well as activities undertaken as part of the ongoing RI work, have delineated chlorinated solvent impacts associated with releases from the Mount Baker Cleaners parcel, including migration of chlorinated solvents downgradient onto the Property.

1.1.2 Summary of Previous Investigations and Remedial Activities

Prior to 2016, a total of 12 soil samples have been collected from multiple excavations and a total of 55 soil borings have been advanced at the Site as part of the former Phillips 66 VCP work. Among these soil borings, 13 have been completed as monitoring wells (7on Property, and 3 off Property) and 5 have been completed as ozone injection wells. The rest were exploratory soil borings.

The RI work completed under the PPCD is ongoing. The RI work to-date has primarily been focused on defining the vertical and lateral extent of both chlorinated solvent and petroleum impacts and developing the Conceptual Site Model (CSM) for the Site. A total of 15 monitoring wells, 32 soil borings (not completed as monitoring wells), 7 soil vapor samples, and 39 groundwater samples have been collected to-date. A summary of the recent RI work is presented in the Aspect *Remedial Investigation Work Plan* dated October 27, 2017 and monthly progress reports are available on the Ecology Site web page.

Reports generated prior to the PPCD documented petroleum and chlorinated solvent impacts at the Property, and further investigation activities undertaken in the last year as part of the ongoing RI have added additional data regarding such impacts. However, the available data has not to-date been adequate to determine if the vapor intrusion pathway for petroleum impacts and chlorinated solvent impacts is complete at the Property, or whether operations at the Property has contributed to the chlorinated solvent impacts to the Site.

A summary of investigation and remedial activities at the Site that precede MBHA's RI activities is included as Appendix A.

2. Rationale for Scope of Work

The objectives for the scope of work are as follows:

- Collect soil vapor data to determine if the vapor intrusion pathway for petroleum impacts and chlorinated solvent impacts is complete at the Property
- Determine whether an onsite release has contributed to the chlorinated solvent impacts to the Site

As presented in Ecology's October 2009 (revised 2016) Guidance for Evaluating Soil Vapor Intrusion in Washington State: Investigation and Remedial Action (VI Guidance) a review of the preliminary groundwater concentration screening criteria for soil vapor intrusion was completed. The evaluation indicates petroleum and chlorinated solvent exceedances of the preliminary groundwater screening levels in several Site monitoring wells. Additionally, American Petroleum Institute's (API) BIOVAPOR – *Indoor Vapor Intrusion Model* was utilized to evaluate the vapor intrusion risk for total petroleum hydrocarbons (TPH) as gasoline (TPHg), TPH as diesel (TPHd),

and benzene, toluene, ethylbenzene, and xylene (BTEX). The results of the preliminary modeling indicated modeled concentrations would be above Ecology's indoor air cleanup levels for aliphatics in the C5 to C8 range and the C9 to C12 range. Therefore, as stated in the VI Guidance, a Tier I vapor assessment is warranted to determine whether the vapor intrusion pathway is complete. A summary of the preliminary soil vapor intrusion evaluation is presented in Appendix B.

The scope of work proposed under this investigation includes collection of soil and soil gas samples at multiple depth intervals. Depth discrete data along with the profile of detected compounds at various locations will be evaluated to determine if there is a potential onsite source or if the most likely source is migration from off-property via either vapor pathways or groundwater.

3. Scope of Work

All work will be conducted according to the Standard Operating Procedures in Section 4 and Appendix C. In addition, reference information from the Interstate Technology Regulatory Council's (ITRC, 2007), California Environmental Protection Agency Department of Toxic Substances Control (Cal EPA, 2012) guidelines, and Ecology Draft Guidance for Evaluating Soil Vapor intrusion in Washington State (Ecology 2009) related to vapor intrusion (VI) pathway evaluation and soil gas investigations also have been used in the preparation of this work plan. The proposed scope of work outlined below is consistent with the rationale described in Section 2.

3.1 Task 1 – Vapor Probe Installation

GHD proposes installing eight vapor probes using a combination of direct-push drill technique or equivalent method to advance one borehole for each vapor probe. Each location will have two vapor probes (shallow and deep). Permanent vapor probes are proposed in the event that additional sampling is necessary. The vapor probes will be decommissioned by GHD within 12 months of installation, or at an earlier date if requested by MBHA. The locations of the proposed vapor probes are presented on Figure 2.

The vapor probe locations, depths, and soil analyses are:

Proposed Vapor Probe Location	Anticipated Soil Samples Per Boring	Anticipated Total Depth / Probe Details	Purpose	Soil Analysis
VP-1-S VP-1-D	1 sample at 5 fbg 1 sample at 10 fbg	6 fbg, Probe screen will be installed at 5 fbg 11 fbg, Probe screen will be installed at 10 fbg*	Investigate soil vapor concentrations based on the location of historical soil and groundwater impacts/on-property building	moisture content, porosity, organic carbon fraction, grain-size distribution, and dry bulk soil density (samples for physical properties analyses will be collected from 3-4 locations across

				that Site that are representative of overall stratigraphy) TPHg, TPHd, BTEX, CVOCs (1 shallow sample in the first five feet and one sample just above the water table or based on field screening)
VP-2-S VP-2-D	1 sample at 5 fbg 1 sample at 10 fbg	6 fbg, Probe screen will be installed at 5 fbg 11 fbg, Probe screen will be installed at 10 fbg*	Investigate soil vapor concentrations based on the location of historical soil and groundwater impacts/on-property building	moisture content, porosity, organic carbon fraction, grain-size distribution, and dry bulk soil density (samples for physical properties analyses will be collected from 3-4 locations across that Site that are representative of overall stratigraphy) TPHg, TPHd, BTEX, CVOCs (1 shallow sample in the first five feet and one sample just above the water table or based on field screening)
VP-3-S VP-3-D	1 sample at 5 fbg 1 sample at 10 fbg	6 fbg, Probe screen will be installed at 5 fbg 11 fbg, Probe screen will be installed at 10 fbg*	Investigate soil vapor concentrations based on the location of historical soil and groundwater impacts/on-property building	moisture content, porosity, organic carbon fraction, grain-size distribution, and dry bulk soil density (samples for physical properties analyses will be collected from 3-4 locations across that Site that are representative of overall stratigraphy)

				TPHg, TPHd, BTEX, CVOCs (1 shallow sample in the first five feet and one sample just above the water table or based on field screening)
VP-4-S VP-4-D	1 sample at 5 fbg 1 sample at 10 fbg	6 fbg, Probe screen will be installed at 5 fbg 11 fbg, Probe screen will be installed at 10 fbg*	Investigate soil vapor concentrations based on the location of historical soil and groundwater impacts/on-property building	moisture content, porosity, organic carbon fraction, grain-size distribution, and dry bulk soil density (samples for physical properties analyses will be collected from 3-4 locations across that Site that are representative of overall stratigraphy) TPHg, TPHd, BTEX, CVOCs (1 shallow sample in the first five feet and one sample just above the water table or based on field screening)
VP-5-S VP-5-D	1 sample at 5 fbg 1 sample at 10 fbg	6 fbg, Probe screen will be installed at 5 fbg 11 fbg, Probe screen will be installed at 10 fbg*	Investigate soil vapor concentrations based on the location of historical soil and groundwater impacts/on-property building	moisture content, porosity, organic carbon fraction, grain-size distribution, and dry bulk soil density (samples for physical properties analyses will be collected from 3-4 locations across that Site that are representative of overall stratigraphy) TPHg, TPHd, BTEX, CVOCs (1 shallow sample in the first five feet and one sample

				just above the water table or based on field screening)
VP-6-S VP-6-D	1 sample at 5 fbg 1 sample at 10 fbg	6 fbg, Probe screen will be installed at 5 fbg 11 fbg, Probe screen will be installed at 10 fbg*	Investigate soil vapor concentrations based on the location of historical soil and groundwater impacts/on-property building	moisture content, porosity, organic carbon fraction, grain-size distribution, and dry bulk soil density (samples for physical properties analyses will be collected from 3-4 locations across that Site that are representative of overall stratigraphy) TPHg, TPHd, BTEX, CVOCs (1 shallow sample in the first five feet and one sample just above the water table or based on field screening)
VP-7-S VP-7-D	1 sample at 5 fbg 1 sample at 10 fbg	6 fbg, Probe screen will be installed at 5 fbg 11 fbg, Probe screen will be installed at 10 fbg*	Investigate soil vapor concentrations based on the location of historical soil and groundwater impacts/on-property building	moisture content, porosity, organic carbon fraction, grain-size distribution, and dry bulk soil density (samples for physical properties analyses will be collected from 3-4 locations across that Site that are representative of overall stratigraphy) TPHg, TPHd, BTEX, CVOCs (1 shallow sample in the first five feet and one sample just above the water table or based on field screening)

VP-8-S VP-8-D	1 sample at 5 fbg 1 sample at 10 fbg	6 fbg, Probe screen will be installed at 5 fbg 11 fbg, Probe screen will be installed at 10 fbg*	Investigate soil vapor concentrations based on the location of historical soil and groundwater impacts/on-property building	moisture content, porosity, organic carbon fraction, grain-size distribution, and dry bulk soil density (samples for physical properties analyses will be collected from 3-4 locations across that Site that are representative of overall stratigraphy) TPHg, TPHd, BTEX, CVOCs (1 shallow sample in the first five feet and one sample just above the water table or based on field screening)

fbg = feet below grade
S = shallow
D = deep
Moisture content by ASTM Method D2216
Soil porosity by ASTM Method D2937
Organic carbon fraction by ASTM Method 2974
Grain size distribution by Sieve Method ASTM D422
Dry bulk soil density by ASTM Method D 2937
TPHg = Gasoline range organics per Method Northwest Total Petroleum Hydrocarbon Identification (NWTPH) Gx
TPHd = Diesel range organics per Method Northwest Total Petroleum Hydrocarbon Identification (NWTPH) Dx
BTEX = Benzene, Toluene, Ethylbenzene and Xylenes per EPA Method 8260B
HVOCs = Halogenated Volatile Organic Carbons per EPA Method 8260B

* = the actual depth of the vapor probes will be dependent upon depth to water encountered in the borings along with measured depth to water in nearby monitoring wells. Modifications to the depths of the probes will be discussed with the project manager prior to installation.

The first 4.5 feet of all borings will be advanced using a hand auger in order to further mitigate contact and damage to potential subsurface utility lines. The borings will then be advanced using a limited access direct push drill rig to the depths noted above. Continuous soil core samples will be collected using 2-inch diameter direct push rods with Macrocore® sampling liners for logging and analysis.

Soil will be continuously logged using the modified Unified Soil Classification System. Soil samples will be screened at approximate 5-foot intervals using a photo ionization detector (PID) and visual inspection. Soil samples will be collected in accordance with Table 3.1 above. The soil collected for physical properties testing will be collected in a Macrocore® liner. A 6-inch section from the depth spanning the center of the screened interval will be cut out of the liner, capped on both ends, sealed with tape to preserve soil moisture, labeled, and sent to PTS laboratories in Houston, TX. Soil samples collected for chemical analyses will be taken from soil immediately above or below the

section removed for soil physical properties testing. The samples for volatile analysis will be collected in accordance with EPA method 5035 using laboratory supplied Terracore™ sample kits. The samples collected for NWTPHDx analysis will be collected in a laboratory supplied sample jar. The samples will be labeled, entered onto a chain of custody form, packed on ice, and sent to Pace Analytical Laboratories in Seattle, WA. A quality Assurance Project Plan (QAPP) detailing the QA/QC procedures, required sample containers, analytical methods, holding times, reporting limits, and preservation methods is presented in Appendix D.

The boreholes will be advanced to the total depths as indicated in the preceding table and will be constructed as clustered boreholes to provide vertical profiles of contaminant concentrations and indicator compounds for aerobic biodegradation. The proposed probe depths account for a buffer zone for capillary actions of approximately 1 foot above the water table. The vapor screens (6 inches long, 0.375 inch OD stainless steel) will be installed and centered at depths of 5 feet bgs for the shallow interval and 10 feet bgs for the deep interval. Teflon, or equivalent, tubing will be connected to the vapor screen and capped with a vapor tight 2-way valve or Swagelok cap at the ground surface. The probe will be installed with the vapor screens emplaced in a 1-foot sand pack (10-20 size), giving a 3-inch layer below and above the screen. The borehole will be backfilled with 1 foot of dry granular bentonite followed by hydrated bentonite up to the surface seal. The surface seal will be a minimum of 1 foot of cement. The same procedures will be repeated for the upper probe with the vapor screen centered at 5 feet bgs. The surface of the probe locations will be completed flush to ground surface with a traffic-rated monument.

GHD's standard operating procedures specifically related to soil vapor sampling, as well as typical vapor probe construction details are presented in Appendix C.

3.2 Task 2 – Vapor Sampling

To allow equilibration of soil vapor, sampling will not be conducted sooner than 2 days after vapor probe installation. Sampling will not be performed during or within 48 hours of a significant rainfall event [e.g., ≥0.5 inches/24 hrs].

Written documentation of all field activities, conditions, and sampling processes, including names of field personnel, dates and times, etc. will be recorded. Documentation will include tenant occupancy, tenant activities including an evaluation of chemical use or emissions, weather conditions (temperature, barometric pressure, wind direction and speed, and humidity), and groundwater depth measurements in monitoring wells.

3.2.1 Pre-Sampling Purge

Prior to sample collection, soil vapor probe purging will be conducted at a flow rate less than 200 milliliters per minute (mL/min). Approximately three soil vapor probe volumes will be purged to remove potentially stagnant air from the internal volume of the soil vapor probe and ensure that soil vapor representative of the formation is drawn into the probe. The soil vapor probe purge volume will be calculated based on probe construction details. Further information regarding purging can be found in Appendix C.

3.2.2 Sample Collection

The soil vapor samples will be collected using 6 liter capacity Summa™ canisters for volatile organic compounds (VOCs). The canisters will be fitted with a laboratory calibrated critical orifice flow regulation device sized to limit the soil vapor sample collection flow rate. Samples will be collected at a flow rate of less than 200 mL/min, which is recommended to limit VOC stripping from soil, prevent the short circuiting of air through the probe seal that may dilute or contaminate the soil vapor sample, and increase confidence regarding the location from which the soil vapor sample is obtained. Sample collection duration will be recorded.

3.2.3 Sample Analysis

The soil vapor samples will be submitted to ALS Environmental Laboratories in Simi Valley, California. The soil vapor samples will be analyzed for VOCs including BTEX, n-hexane, 1,2 dibromoethane (ethylene dibromide), 1,2 dichloroethane, naphthalene, 1,3,5 trimethylbenzene, and 1,2,4 trimethylbenzene, Tetrachloroethylene, Trichloroethylene, Cis-1,2 Dichloroethene, and Vinyl Chloride, using EPA Method TO 15; and TPH fractions using Massachusetts Air Phase Hydrocarbons (APH) Method. Samples will also be analyzed for biodegradation indicator gases including oxygen, carbon dioxide, and methane by ASTM Method D1946; and tracer helium by EPA 3C modified. Canisters will be batch certified in accordance with standard laboratory reporting protocol for EPA Method TO 15 and APH Method.

3.2.4 Quality Assurance / Quality Control

Quality assurance/quality control (QA/QC) measures implemented during the soil vapor sampling event will include leak testing, maintaining a minimum residual negative pressure in the Summa™ canisters of approximately 1 to 5 inches of mercury following sample collection, collection of one field duplicate sample and one ambient air/blank sample. Further details regarding the soil vapor probe sampling QA/QC measures, required sample containers, analytical methods, holding times, reporting limits and preservation methods are presented in Appendix D. A brief description of the leak testing procedures is provided below.

Leak testing will be performed to determine whether ambient air has infiltrated the sample collection system during sampling. The leak testing will consist of a two-step process. The first step, conducted prior to sample collection, will involve vacuum testing the sampling equipment after assembly to test the air tightness of the assembly connections. The second step, conducted prior to sample collection, will involve leak detection of the soil vapor probe using helium as a tracer compound and above ground sampling assembly connections to the soil vapor probe.

Leak Testing Step One

The sampling assembly will be connected to include the purge pump and an in-line vacuum gauge in valved tee connections before connecting to the Summa™ canister. Prior to purging the vapor probe, the valve to the purge pump will be opened leaving closed the valve on the Summa™ canister and the valve to the vapor probe. The pump will be operated to create a vacuum within the sampling assembly. The vacuum will be held for 1 minute (recording vacuum gauge readings at the beginning and end of test). If the vacuum is maintained the assembly connections will be considered air tight. Purging of the vapor probe will then commence. Once purging is completed,

the valve to the purge pump will be closed, and the second leak test step described below will be implemented. The valve to the Summa™ canister will then be opened and sample collection will commence.

Leak Testing Step Two

A shroud (i.e. clear plastic box) will be placed atop the soil vapor probe. Helium gas will be introduced within the shroud via tubing, and the helium concentration under the shroud will be measured using a helium meter (parts per billion detection level), and recorded as a percentage. The helium meter will then be connected to the soil vapor probe sampling assembly to monitor for leaks during sample collection. Detection of helium within the sampling assembly of greater than 5 percent of the helium concentration beneath the shroud will be considered indicative of a substantial leak that would compromise the soil vapor sample. Should this occur, the sampling assembly should be dismantled and then re-assembled. The leak testing procedure will be repeated. In the event that the leak testing fails a second time, the probe should be decommissioned and replaced.

3.3 Task 3 – Groundwater Sampling

Concurrent groundwater samples will be collected from monitoring wells MW-1, MW-8, MW-9, MW-11, MW-13, AMW-4, and AMW-5. Each well will be gauged and sampled using low-flow sampling procedures. One duplicate sample and on MS/MSD sample will be collected. Groundwater samples will be sent to Pace Analytical Laboratories in Seattle, Washington under chain of custody and analyzed for TPHg per Ecology Method NWTPH-Gx, TPHd and TPH as oil (TPHo) per Ecology Method NWTPH-Dx, and BTEX and chlorinated solvents per EPA Method 8260 (8260B SIM if necessary to meet reporting limits). A quality Assurance Project Plan (QAPP) detailing the QA/QC procedures, required sample containers, analytical methods, holding times, reporting limits, and preservation methods is presented in Appendix D.

4. Standard Operating Procedures

The following standard operating procedures will be used, based on the proposed scope of work with possible deviations to the identified scope predicated on field observations of current site conditions.

4.1 Health and Safety Plan

GHD will prepare a comprehensive site specific Health and Safety Plan to protect site workers. The plan will be reviewed and signed by each site worker and kept on site during field activities.

4.2 Utility Clearance

Each proposed boring location will be cleared through Washington Utilities Coordinating Council (WUCC) prior to drilling. A private utility locating service will also be used to verify clearance of each boring from subsurface utilities or other obstructions. During work, each boring will be cleared to total depth of 5 fbg with a diameter of 3 inches larger than the probe using a hand auger to minimize

potential damage to underground structures not identified through WUCC or the private utility locating service. The final boring locations will be based on the utility clearance.

4.3 Investigation-Derived Waste

Investigation-derived waste (IDW) will include one or more of the following: personal protective equipment, decontamination fluids, and soil cuttings from borings. All IDW will be placed in properly labeled 55-gallon drums and stored on-site pending analyses. The IDW will be disposed of according to SOPUS procedures and applicable regulatory requirements.

4.4 Certification

The scope of work described in this work plan will be performed under the supervision of a Washington state licensed geologist.

4.5 References

GHD. 2015. Draft Remedial Investigation/Feasibility Study Report. 2015

American Petroleum Institute (API). 2010. BioVapor Version 2.0.

California Environmental Protection Agency – Department of Toxic Substances Control. 2012. Advisory Active Soil Gas Investigations. April.

Interstate Technology & Regulatory Council. 2007. Vapor Intrusion Pathway: A Practical Guideline. ITRC Vapor Intrusion Team, Washington D.C. January.

Washington State Department of Ecology. 2009. Guidance for Evaluating Soil Vapor Intrusion in Washington State: Investigation and Remedial Action, Review Draft. October 2009. Revised 2016.

All of Which is Respectfully Submitted,

GHD

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Figures

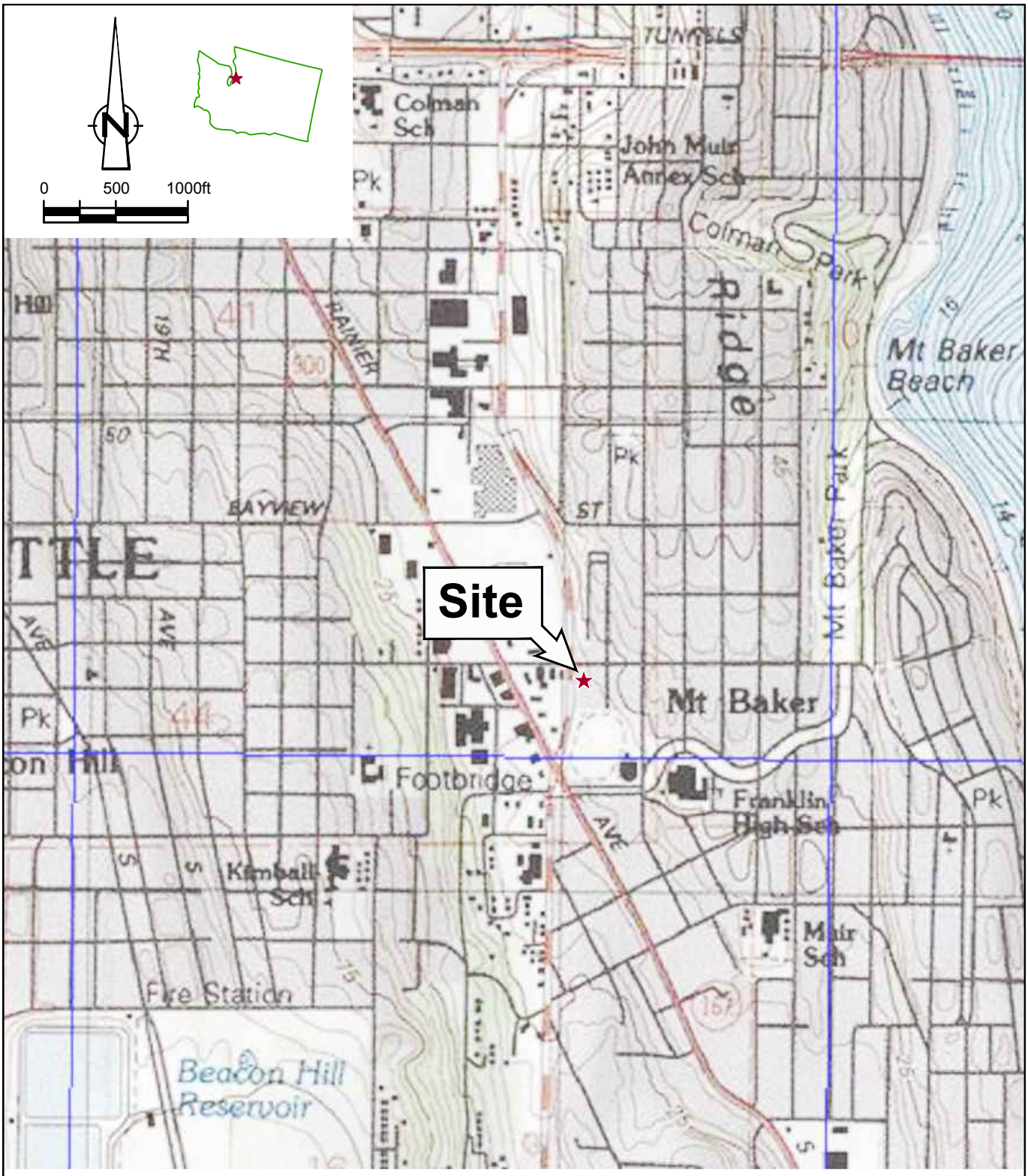

figure 1

VICINITY MAP
FORMER TIDEWATER SERVICE STATION
PHILLIPS 66 SITE 5173
CHEVRON SITE 301233
2800 MARTIN LUTHER KING WAY SOUTH
Seattle, Washington

GHD

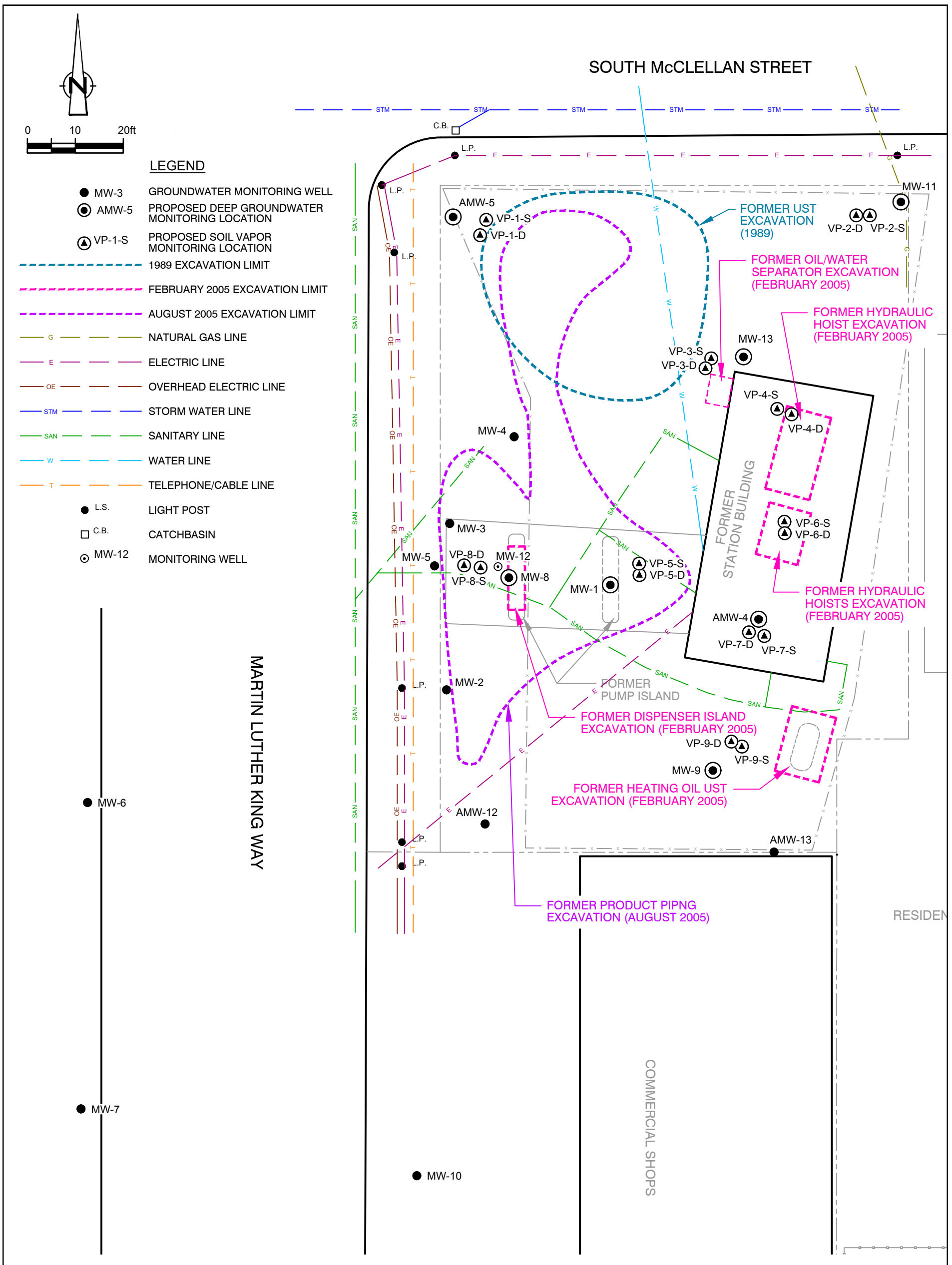

figure 2

SITE PLAN
FORMER TIDEWATER SERVICE STATION
PHILLIPS 66 SITE 5173
CHEVRON SITE 301233
2800 MARTIN LUTHER KING WAY SOUTH
Seattle, Washington

GHD

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Appendices

Appendix A
Summary of Previous Site Investigations and Remedial Activities

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1989 UST Removal: In 1989, one 4,000-gallon gasoline underground storage tanks (UST), one 5,000-gallon gasoline UST, one 300-gallon waste oil UST, and one dispenser island were excavated and removed. Soil samples were collected from the extents of the excavation. One soil sample collected from top of the 4,000-gallon UST was reported to contain a concentration of total petroleum hydrocarbon (TPH) as gasoline (TPHg) at 90 milligrams per kilogram (mg/kg), which was below Washington State Department of Ecology (Ecology)'s Model Toxics Control Act (MTCA) Method A cleanup level of 100 mg/kg. No other samples collected had concentrations exceeding the laboratory detection limits.

2005 Phase I Environmental Site Assessment: In 2005, The G-Logics, Inc. (G-Logics) completed a Phase I at the Property. Results of the assessment identified the following environmental conditions:

- Product piping and west dispenser island were still in place and were not removed during the 1989 excavation.
- Two underground hydraulic hoists were present in the service bays. The tenant indicated that one hoist required periodic addition of fluid due to a leak.
- A garage floor drain sump and oil/water separator contained emulsified oil and water. The tenant indicated that the oil/water separator had not been cleaned in the 3 years he had operated at the property.
- An underground heating oil tank is present on the south side of the building. The state of the tank could not be determined.
- It is not clear whether the former UST pit had been backfilled with contaminated soils.
- A dry cleaning facility up-gradient from the Site could be a potential source of soil and groundwater contamination.

Additional information is available in G-Logics' *Phase I Environmental Assessment,* dated January 11, 2005.

2005 Phase II Environmental Assessment: In February 2005, G-Logics oversaw the decommissioning of the remaining west dispenser island and piping, the two hydraulic hoists, the oil/water separator, the floor drain sump, and the 270-gallon heating oil UST. Approximately 0.5 cubic yard of petroleum hydrocarbon impacted soils were encountered in the hydraulic hoist excavation and placed into stockpile SP-2. One soil sample collected from soil SP-2 contained concentration of TPH as diesel (TPHd) at 2,200 mg/kg, which was above the MTCA Method A cleanup level. Soil samples collected from the bottom of all excavations contained petroleum hydrocarbon constituents concentrations below MTCA Method A cleanup levels. Two test pits were excavated to approximately 2 feet below ground surface (bgs) at the former west dispenser island and soil samples collected from the bottom of the test pits were below MTCA Method A cleanup levels. The excavations and test pits were backfilled with excavated soils. The soils from the stockpile SP-2 were placed in the upper 2 feet of the hoist excavation.

G-Logics also oversaw the installation of six soil borings GL-1 through GL-6 to the maximum depth of 20.5 feet bgs in the vicinity of former USTs, oil/water separator, and dispenser islands. Petroleum hydrocarbon concentrations in the soil samples collected from the borings were all below MTCA Method A cleanup levels. Grab groundwater samples were collected from boring GL-1 and GL-4. The groundwater

sample collected from boring GL-4 contained TPHg concentration at 5,900 µg/L exceeding the MTCA Method A cleanup level. Additional information is available in G-Logics' *Phase II Environmental Assessment,* dated March 17, 2005.

2005 Additional Site Investigation: G-Logics conducted an additional investigation including advancing 11 soil borings P1 through P11 in the vicinity of former west dispenser island near boring GL-4 in June 2005. Soil samples collected from borings P1, P3, P-6, P-7, P-8, P-9, and P-10 between depths of 15 and 18 feet bgs contained concentrations of TPHg or benzene, toluene, ethylbenzene, total xylenes (BTEX) exceeding MTCA Method A cleanup levels. The investigation is summarized in G-Logics' *Summary Report - Site Remediation and Groundwater Monitoring,* dated August 2, 2007.

2005 Remedial and Investigation Activities: In August 2005, G-Logics conducted remedial activities and additional investigation at the site including the following:

- Remove most of the concrete surface in the former dispenser islands area. Remove and dispose remaining product fuel lines and excavate soils from the former dispenser islands and product line trench.
- Install three monitoring wells MW-1 through MW-3 and conduct groundwater sampling.
- Install an ozone soil and groundwater remediation system and start up the system.

Soil removal excavations at the former dispenser islands and product line trench were completed to an average depth of 3 feet bgs. Four soil samples were collected from the bottom and sidewalls of the excavations. Two composite samples were taken from the stockpiled soils. All soil samples including the stockpile samples did not contain petroleum hydrocarbon concentrations above MTCA Method A cleanup levels. The clean stockpile soils were used as backfill.

Three groundwater monitoring wells were installed on the west portion of the property near former dispenser islands: well MW-1 was installed adjacent to the former eastern dispenser island; wells MW-2 and MW-3 were installed on the western edge of the property adjacent to the Martin Luther King Way sidewalk. Soil samples were not collected from the wells; groundwater samples collected from wells MW-2 and MW-3 contained concentrations of TPHg and/or BTEX constituents above MTCA Method A cleanup levels.

Five ozone injection points IP-1 through IP-5 were installed at former dispenser islands area on the western portion of the property. The ozone injection system began operation on August 26, 2005.

Additional information is available in G-Logics' *Cleanup Action Report,* dated October 31, 2005.

2006 Additional Investigation: G-Logics installed additional soil borings P-12 through P-16 and monitoring wells MW-4 and MW-5 in the vicinity and up-gradient of MW-3 in June 2006 due to elevated concentrations of TPHg detected in tMW-3. One soil sample collected at 20 feet bgs from well MW-5 contained a benzene concentration at 0.03 mg/kg, equaling to the MTCA Method A cleanup levels. All other soil samples collected from all borings were below MTCA Method A cleanup levels. Groundwater samples collected from well MW-5 contained concentrations of TPHg and/or BTEX above MTCA Method A cleanup levels. The investigation is summarized in G-Logics' *Summary Report - Site Remediation and Groundwater Monitoring,* dated August 2, 2007.

2006 to 2007 Remediation System Operation: In July 2006, ozone flow to injection points IP-1, IP-2, and IP-3 was stopped. All flow from the ozone injection system was directed towards injection points IP-4 and IP-5, in the area near MW-3.

In August 2006, a second compressor was added to augment the ozone injection system. The second compressor was dedicated to providing a primary source of air flow to the wells; the original compressor was dedicated to providing air flow to the ozone generator.

To supplement the ozone treatment system, in December 2006, G-Logics oversaw the installation of a horizontal pipe for In-Situ Chemical Oxidation (ISCO) in an area up-gradient of the western dispenser island. The pipe was installed at approximately 6 to 7 feet; installation at a greater depth was unfeasible due to soil caving. Between January and March 2007, ISCO using Fenton's Reagent was performed to supplement ozone injection remediation efforts. On January 4, 2007, a buffered, iron-catalyst was introduced with the Fenton's application. In March 2007, a Fenton's application treatment well (TW-1) was installed directly west of the west pump island source area. The ozone system was shut down in June 2007. Additional information is available in G-Logics' *Summary Report - Site Remediation and Groundwater Monitoring,* dated August 2, 2007.

2011 Soil and Groundwater Assessment: In April 2011, Stantec Consulting Corporation (Stantec) oversaw the installation of seven soil borings B-1 through B-7 to maximum depth of 20 feet bgs on the western portion of the property and adjacent to the former heating oil UST. Soil samples collected from borings B-2, B-3, B-6 and B-7 between depths of 10 and 17 feet bgs contained concentrations of TPHg or TPHd above MTCA Method A cleanup levels.

In July 2011, Stantec oversaw the installation of five groundwater monitoring wells MW-6 through MW-10. Among these, wells MW-6, MW-7, and MW-10 were off-property wells. Wells MW-6 through MW-8, and MW-10 were installed with a total depth of 20 feet bgs and screened from 10 to 20 feet bgs; well MW-9 was installed with a total depth of 25 feet bgs and screened from 10 to 25 feet bgs. The soil sample collected from well MW-8 at 15 feet bgs contained a TPHg concentration above MTCA Method A cleanup levels. Soil samples collected from well MW-9 from 10 to 15 feet bgs contained TPHo and carcinogenic polycyclic aromatic hydrocarbons (cPAHs) concentrations exceeding MTCA Method A cleanup levels. Groundwater samples collected from borings B-1 through B-7 and monitoring wells MW-2, MW-3, MW-5 and MW-8 contained concentrations of one or more petroleum hydrocarbon constituents exceeding MTCA Method A cleanup levels. Additional information is available in Stantec's *Soil and Groundwater Assessment Report,* dated March 14, 2012.

2014 and 2015 Site Investigation: In June 2014, GHD advanced nine soil borings via a hollow stem auger drill rig. Among these, six of the borings were exploratory soil borings advanced to a total depth of approximately 20 feet bgs on the southern and northwestern portions of the Property. These borings were designated as B-8 through B-12, and B-15. Three of the borings were completed as monitoring wells MW-11, MW-12, and MW-13 on the northeastern and western portions of the Property. Monitoring wells MW-11 and MW-13 were completed as 2-inch diameter wells with a total depth of 20 feet bgs screened from 10 to 20 feet bgs for the purpose of groundwater monitoring to verify the presence of an up-gradient source of chlorinated solvents. Boring MW-12 was advanced to 30 feet bgs to confirm the total depth of the water bearing zone. The total depth of the water bearing zone was determined to be 20 feet bgs. The boring was completed as a 4-inch diameter well with a total depth of 25 feet bgs including a 5-foot sump, screened from 5 to 20 feet bgs or approximately across the shallow groundwater production zone for the purpose of a groundwater yield test.

In March 2015, GHD advanced two additional soil borings B-13 and B-14 to a total depth of 20 feet bgs via a direct push drill rig. The two soil borings were advanced inside the former auto detailing building near the former hoist excavation and floor drain sump.

2015 Yield Test: In January 2015, GHD performed a yield test on monitoring well MW-2 to test the portability of shallow groundwater at the site. The results indicate that shallow groundwater is likely

present in sufficient quantity to yield greater than 0.5 gallon per minute (gpm) on a sustainable basis (24-hour period).

Appendix B

Summary of Preliminary Soil Vapor Intrusion Evaluation

Table B.1

Groundwater Data for Vapor Intrusion Screening
Former Tidewater Site
Phillips 66 Site 5173
Chevron Site 301233
2800 Martin Luther King Junior Way South
Seattle, Washington

		Petroleum Hydrocarbons Constituents								Chlorinated Solvents		
Location	**Date**	**TPHg**	**TPHd**	**TPHo**	**B**	**T**	**E**	**X**	**Naphthalene**	**PCE**	**TCE**	**VC**
MTCA Method B groundwater screening levels for vapor intrusion		**NE**	**NE**	**NE**	**2.4**	**15,600**	**2,780**	**310***	**8.93**	**22.9**	**1.55**	**0.347**
		µg/L	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**
MW-1	08/19/2005	ND	--	--	ND	ND	ND	ND	--	--	--	--
MW-1	10/27/2005	ND	--	--	ND	ND	ND	ND	--	--	--	--
MW-1	12/27/2005	ND	--	--	ND	ND	ND	ND	--	--	--	--
MW-1	01/12/2006	--	--	--	--	--	--	--	--	--	--	--
MW-1	03/02/2006	ND	--	--	ND	ND	ND	ND	--	--	--	--
MW-1	06/28/2006	--	--	--	--	--	--	--	--	--	--	--
MW-1	12/01/2006	--	--	--	--	--	--	--	--	--	--	--
MW-1	12/06/2006	--	--	--	--	--	--	--	--	--	--	--
MW-1	02/28/2007	--	--	--	--	--	--	--	--	--	--	--
MW-1	03/07/2007	--	--	--	--	--	--	--	--	--	--	--
MW-1	04/11/2007	ND	--	--	ND	ND	ND	ND	--	--	--	--
MW-1	11/12/2009	<50	--	--	<1.0	<1.0	<1.0	<3.0	--	--	--	--
MW-1	08/30/2011	Well not sampled - well not found							--	--	--	--
MW-1	12/15/2011	Well not sampled - well not found							--	--	--	--
MW-1	02/06/2012	260	430	620	<0.5	41	3	18	<1	--	--	--
MW-1	05/30/2012	<50	35	170	<0.5	<0.7	<0.8	<0.8	<1	9	**13**	<1 b
MW-1	08/08/2012	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	5	**9**	**1**
MW-1	12/05/2012	<50	<29 a	<69 a	<0.5	<0.5	<0.5	<0.5	<1	6	**8**	**4**
MW-1	02/26/2013	<50	<30 a	<71 a	<0.5	<0.5	<0.5	<0.5	<1	5	**6**	**1**
MW-1	05/23/2013	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	10	**9**	<1 b
MW-1	08/29/2013	<50	<29 a	<67 a	<0.5	<0.5	<0.5	0.8	<1	7	**6**	<1 b
MW-1	11/13/2013	<50	<32 a	<74 a	<0.5	<0.5	<0.5	<0.5	<1	7	**6**	<1 b
MW-1	03/19/2014	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	7	**6**	**1**
MW-1	05/27/2014	<50	<28 a	<66 a	<0.5	<0.5	<0.5	<0.5	<1	5	**4**	**2**
MW-1	08/28/2014	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	6	**6**	**0.9 J**
MW-1 DUP	08/28/2014	<50	<29	<67	<0.5	<0.5	<0.5	<0.5	<1	6	**6**	**1**
MW-1	12/11/2014	<50	<29	<67	<0.5	<0.5	<0.5	<0.5	<1	4	**5**	**1 J**
MW-1	03/12/2015	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	5	**5**	<0.5 b
MW-2	08/19/2005	2,000	--	--	ND	10	81	91	--	--	--	--
MW-2	10/27/2005	2,300	--	--	ND	ND	89	93	--	--	--	--
MW-2	12/27/2005	820	--	--	ND	ND	21	66	--	--	--	--

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Former Tidewater Site
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Chevron Site 301233
2800 Martin Luther King Junior Way South
Seattle, Washington

		Petroleum Hydrocarbons Constituents								Chlorinated Solvents		
Location	**Date**	**TPHg**	**TPHd**	**TPHo**	**B**	**T**	**E**	**X**	**Naphthalene**	**PCE**	**TCE**	**VC**
MTCA Method B groundwater screening levels for vapor intrusion		**NE µg/L**	**NE µg/L**	**NE µg/L**	**2.4 µg/L**	**15,600 µg/L**	**2,780 µg/L**	**310* µg/L**	**8.93 µg/L**	**22.9 µg/L**	**1.55 µg/L**	**0.347 µg/L**
MW-2	01/12/2006	--	--	--	-	-	-	-	--	--	--	--
MW-2	03/02/2006	1,300	--	--	ND	3.9	23	50	--	--	--	--
MW-2	04/13/2006	470	--	--	ND	1.4	6.9	15	--	--	--	--
MW-2	06/28/2006	--	--	--	-	-	-	-	--	--	--	--
MW-2	09/11/2006	580	--	--	ND	1.6	2.9	6.2	--	--	--	--
MW-2	12/01/2006	--	--	--	-	-	-	-	--	--	--	--
MW-2	12/06/2006	--	--	--	-	-	-	-	--	--	--	--
MW-2	01/12/2007	--	--	--	-	-	-	-	--	--	--	--
MW-2	02/12/2007	1,400	--	--	1.4	3.5	16	13	--	--	--	--
MW-2	02/28/2007	1,200	--	--	2	4	18	60	--	--	--	--
MW-2	03/07/2007	--	--	--	-	-	-	-	--	--	--	--
MW-2	04/11/2007	1,200	--	--	ND	3	11	63	--	--	--	--
MW-2	11/12/2009	455	--	--	<1.0	<1.0	<1.0	<3.0	--	--	--	--
MW-2	08/31/2011	960	590	--	1	<0.7	1	6	<1	--	--	--
MW-2	12/15/2011	750	30	--	1	<0.7	1	<1.6	<1	--	--	--
MW-2	02/06/2012	780	390	--	1	2	<0.8	<1.6	<1	--	--	--
MW-2	05/30/2012	480	210	<67	0.8	<0.7	<0.8	<0.8	<1	<0.8	<1	<1 b
MW-2	08/08/2012	670	160 a	<67 a	0.9	<0.5	<0.5	0.5	<1	<0.8	<1	<1 b
MW-2	12/05/2012	590	250 a	<73 a	2	<0.5	3	11	<1	<0.8	<1	<1 b
MW-2	02/26/2013	770	150 a	<68 a	0.7	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-2	05/23/2013	470	200 a	<66 a	0.7	<0.5	<0.5	3	<1	<0.8	<1	<1 b
MW-2	08/29/2013	740	200 a	<67 a	0.6	<0.5	<0.5	<0.5	1	<0.8	<1	<1 b
MW-2	11/13/2013	700	160 a	<67 a	1	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-2	03/18/2014	870	180 a	<66 a	0.9	<0.5	3	2	<1	<0.8	<1	<1 b
MW-2	05/27/2014	370	300 a	<66 a	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-2	08/28/2014	440	270	<66	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-2	12/11/2014	420	170	<66	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-2	03/12/2015	360	330	<67	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-3	08/19/2005	44,000	--	--	**4.1**	18	780	**3,600**	--	--	--	--
MW-3	12/27/2005	17,000	--	--	ND	38	580	**3,000**	--	--	--	--
MW-3	12/28/2005	6,600	--	--	**5**	22	200	**1,100**	--	--	--	--

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Chevron Site 301233
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Seattle, Washington

		Petroleum Hydrocarbons Constituents								Chlorinated Solvents		
Location	**Date**	**TPHg**	**TPHd**	**TPHo**	**B**	**T**	**E**	**X**	**Naphthalene**	**PCE**	**TCE**	**VC**
MTCA Method B groundwater screening levels for vapor intrusion		**NE µg/L**	**NE µg/L**	**NE µg/L**	**2.4 µg/L**	**15,600 µg/L**	**2,780 µg/L**	**310* µg/L**	**8.93 µg/L**	**22.9 µg/L**	**1.55 µg/L**	**0.347 µg/L**
MW-3	01/12/2006	-	--	--	-	-	-	-	--	--	--	--
MW-3	03/02/2006	22,000	--	--	ND	26	450	**4,200**	--	--	--	--
MW-3	04/13/2006	33,000	--	--	ND	3	700	**3,100**	--	--	--	--
MW-3	06/28/2006	53,000	--	--	ND	17	530	**2,600**	--	--	--	--
MW-3	08/13/2006	-	--	--	-	-	-	-	--	--	--	--
MW-3	09/11/2006	14,000	--	--	ND	5.6	180	**1,100**	--	--	--	--
MW-3	10/13/2006	1,400	--	--	ND	1	26	98	--	--	--	--
MW-3	11/17/2006	48,000	--	--	ND	34	490	**4,100**	--	--	--	--
MW-3	12/01/2006	-	--	--	-	-	-	-	--	--	--	--
MW-3	12/06/2006	-	--	--	-	-	-	-	--	--	--	--
MW-3	01/12/2007	-	--	--	-	-	-	-	--	--	--	--
MW-3	02/12/2007	36,000	--	--	ND	10	280	**1,800**	--	--	--	--
MW-3	02/28/2007	22,000	--	--	ND	6	200	**1,400**	--	--	--	--
MW-3	03/07/2007	21,000	--	--	ND	18	170	**1,000**	--	--	--	--
MW-3	04/11/2007	19,000	--	--	ND	6	110	**1,100**	--	--	--	--
MW-3	11/12/2009	71.7	--	--	ND	<1.0	<1.0	<3.0	--	--	--	--
MW-3	08/31/2011	7,400	370	<68	<1.0	<1	190	554	**67**	--	--	--
MW-3	12/15/2011	5,400	<29	<67	<0.5	<0.7	120	400	**50**	--	--	--
MW-3	02/06/2012	6,300	1,200	<68	<1	<1	130	523	**49**	--	--	--
MW-3	05/30/2012	7,400	520	<66	<1	<1	160	660	**66**	<2	<2	<2 b
MW-3	08/07/2012	8,100	290 a	<67 a	<1	<1	140	610	**71**	<2	<2	<2 b
MW-3	12/06/2012	6,700	290 a	<69 a	<0.5	<0.5	160	480	**75**	<0.8	<1	<2 b
MW-3	02/27/2013	9,500	510 a	<66 a	<0.5	<0.5	190	620	**73**	<0.8	<1	**1**
MW-3	05/23/2013	5,800	240 a	<67 a	<0.5	<0.5	160	550	**82**	<0.8	<1	**2**
MW-3	08/30/2013	4,300	260 a	<70 a	<0.5	<0.5	54	190	**33**	<0.8	<1	**1**
MW-3	11/13/2013	3,100	120 a	<67 a	<0.5	<0.5	33	120	**20**	<0.8	<1	**1**
MW-3	03/19/2014	6,300	180 a	<66 a	<0.5	<0.5	100	410	**49**	<0.8	<1	**1**
MW-3	05/27/2014	8,700	210 a	<66 a	<1	<1	180	460	**54**	<1	<1	<1 b
MW-3	08/29/2014	2,800	170	<66	<0.5	<0.5	34	34	**9**	<0.5	<0.5	<0.5 b
MW-3	12/11/2014	7,800	150	<67	<1	<1	150	510	**69**	<1	<1	<1 b
MW-3	03/13/2015	7,700	310	<67	<1	<1	160	360	**54**	<1	<1	<1 b
MW-3 DUP	03/13/2015	7,500	240	<66	<0.5	0.8 J	190	420	**61**	<0.5	<0.5	<0.5 b

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		Petroleum Hydrocarbons Constituents								Chlorinated Solvents		
Location	**Date**	**TPHg**	**TPHd**	**TPHo**	**B**	**T**	**E**	**X**	**Naphthalene**	**PCE**	**TCE**	**VC**
MTCA Method B groundwater screening levels for vapor intrusion		**NE µg/L**	**NE µg/L**	**NE µg/L**	**2.4 µg/L**	**15,600 µg/L**	**2,780 µg/L**	**310* µg/L**	**8.93 µg/L**	**22.9 µg/L**	**1.55 µg/L**	**0.347 µg/L**
MW-4	06/28/2006	ND	--	--	ND	ND	ND	ND	--	--	--	--
MW-4	12/01/2006	--	--	--	--	--	--	--	--	--	--	--
MW-4	12/06/2006	--	--	--	--	--	--	--	--	--	--	--
MW-4	02/28/2007	--	--	--	--	--	--	--	--	--	--	--
MW-4	03/07/2007	ND	--	--	ND	ND	ND	ND	--	--	--	--
MW-4	04/11/2007	ND	--	--	ND	ND	ND	ND	--	--	--	--
MW-4	11/12/2009	<50	--	--	<1.0	<1.0	<1.0	<3.0	--	--	--	--
MW-4	08/31/2011	<50	<29	<68	<0.5	<0.7	<0.8	<0.8	<1	--	--	--
MW-4	12/15/2011	<50	<29	<67	<0.5	<0.7	<0.8	<1.6	<1	--	--	--
MW-4	02/06/2012	<50	55	<67	<0.5	<0.7	<0.8	<1.6	<1	--	--	--
MW-4	05/30/2012	<50	<29	<67	<0.5	<0.7	<0.8	<0.8	<1	<0.8	<1	<1 b
MW-4	08/07/2012	<50	<29 a	<68 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-4	12/05/2012	<50	<32 a	<75 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-4	02/26/2013	<50	<28 a	<66 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-4	05/23/2013	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-4	08/29/2013	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-4	11/13/2013	<50	<31 a	<73 a	<0.5	<0.5	0.5	<0.5	<1	<0.8	<1	<1 b
MW-4	03/18/2014	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-4	05/27/2014	<50	<28 a	<66 a	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-4	08/28/2014	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-4	12/10/2014	<50	<29	<67	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-4 DUP	12/10/2014	<50	<28	<65	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-4	03/13/2015	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-5	06/28/2006	21,000	--	--	ND	14	290	**920**	--	--	--	--
MW-5	09/11/2006	2,500	--	--	ND	ND	34	60	--	--	--	--
MW-5	11/17/2006	23,000	--	--	ND	52	450	**1,700**	--	--	--	--
MW-5	12/01/2006	--	--	--	--	--	--	--	--	--	--	--
MW-5	01/12/2007	--	--	--	--	--	--	--	--	--	--	--
MW-5	02/12/2007	37,000	--	--	ND	33	1,600	**2,800**	--	--	--	--
MW-5	02/28/2007	29,000	--	--	ND	24	550	**1,800**	--	--	--	--

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		Petroleum Hydrocarbons Constituents								Chlorinated Solvents		
Location	**Date**	**TPHg**	**TPHd**	**TPHo**	**B**	**T**	**E**	**X**	**Naphthalene**	**PCE**	**TCE**	**VC**
MTCA Method B groundwater screening levels for vapor intrusion		**NE**	**NE**	**NE**	**2.4**	**15,600**	**2,780**	**310***	**8.93**	**22.9**	**1.55**	**0.347**
		µg/L	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**
MW-5	03/07/2007	42,000	--	--	11	24	740	**2,500**	--	--	--	--
MW-5	04/11/2007	65,000	--	--	ND	79	850	**4,000**	--	--	--	--
MW-5	11/12/2009	2,340	--	--	1	36	<1.0	125	--	--	--	--
MW-5	08/31/2011	3,100	770	<67	2	1	72	124	**120**	--	--	--
MW-5	12/15/2011	1,900	66	<67	1	0.9	24	33	**81**	--	--	--
MW-5	02/06/2012	1,200	34	<68	0.8	<0.7	12	43	**37**	--	--	--
MW-5	05/30/2012	260	54	<66	<0.5	<0.7	3	7	**12**	<0.8	<1	<1 b
MW-5	08/07/2012	610	190 a	<66 a	<0.5	<0.5	11	22	**21**	<0.8	<1	<1 b
MW-5	12/06/2012	170	40	<76 a	<0.5	<0.5	2	8	8	<0.8	<1	<1 b
MW-5	02/27/2013	790	170 a	<69 a	<0.5	0.6	7	12	**25**	<0.8	<1	<1 b
MW-5	05/23/2013	360	64 a	<67 a	<0.5	<0.5	4	6	**25**	<0.8	<1	<1 b
MW-5	08/30/2013	3,200	340 a	<69 a	0.7	1	49	89	**92**	<0.8	<1	<1 b
MW-5	11/14/2013	2,000	240 a	<75 a	0.7	0.7	19	14	**54**	<0.8	<1	<1 b
MW-5	03/19/2014	1,700	110 a	<67 a	<0.5	<0.5	34	150	**26**	<0.8	<1	<1 b
MW-5	05/28/2014	570	100 a	<67 a	<0.5	<0.5	8	26	**9**	0.5	<0.5	<0.5 b
MW-5	08/28/2014	3,900	360	<66	<0.5	0.9 J	34	65	**36**	<0.5	<0.5	<0.5 b
MW-5	12/11/2014	260	<29	<67	<0.5	<0.5	0.8 J	5	1 J	0.6 J	<0.5	<0.5 b
MW-5	03/13/2015	670	170	<66	<0.5	<0.5	5	5	2 J	0.5 J	<0.5	<0.5 b
MW-6	08/31/2011	<50	44	<67	<0.5	<0.7	<0.8	<0.8	1	--	--	--
MW-6	12/15/2011	<50	<29	<67	<0.5	<0.7	<0.8	<1.6	<1	--	--	--
MW-6	02/06/2012	<50	<29	<68	<0.5	<0.7	<0.8	<1.6	<1	--	--	--
MW-6	05/30/2012	<50	<29	<68	<0.5	<0.7	<0.8	<0.8	<1	<0.8	<1	<1 b
MW-6	08/07/2012	<50	<28 a	<66 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-6	12/06/2012	<50	<31 a	<73 a	<0.5	<0.5	1	6	<1	<0.8	<1	<1 b
MW-6	02/27/2013	<50	<30 a	<70 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-6	05/24/2013	<50	<30 a	<70 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-6	08/29/2013	<50	<28 a	<66 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-6	11/14/2013	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-6	03/18/2014	<50	<29 a	<68 a	**4**	<0.5	<0.5	<0.5	<1	<0.8	<1	<1 b
MW-6	05/28/2014	<50	<28 a	<66 a	1	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-6	08/29/2014	<50	59 J	120 J	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b

Table B.1

Groundwater Data for Vapor Intrusion Screening
Former Tidewater Site
Phillips 66 Site 5173
Chevron Site 301233
2800 Martin Luther King Junior Way South
Seattle, Washington

		Petroleum Hydrocarbons Constituents								Chlorinated Solvents		
Location	**Date**	**TPHg**	**TPHd**	**TPHo**	**B**	**T**	**E**	**X**	**Naphthalene**	**PCE**	**TCE**	**VC**
MTCA Method B groundwater screening levels for vapor intrusion		**NE**	**NE**	**NE**	**2.4**	**15,600**	**2,780**	**310***	**8.93**	**22.9**	**1.55**	**0.347**
		µg/L	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**
MW-6	12/10/2014	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-6	03/13/2015	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	<0.5 b
MW-7	08/31/2011	<50	<29	<67	<0.5	<0.7	<0.8	<0.8	<1	--	--	--
MW-7	12/15/2011	<50	45	89	<0.5	<0.7	<0.8	<1.6	<1	--	--	--
MW-7	02/06/2012	<50	<29	<68	<0.5	2	<0.8	<1.6	<1	--	--	--
MW-7	05/30/2012	<50	37	160	<0.5	<0.7	<0.8	<0.8	<1	<0.8	**3**	**3**
MW-7	08/07/2012	<50	<28 a	<66 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	**4**
MW-7	12/06/2012	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	**7**
MW-7	02/27/2013	<50	<29 a	<68 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	**2**	**3**
MW-7	05/24/2013	<50	<31 a	<72 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	**2**	**5**
MW-7	08/29/2013	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	3	**5**	**3**
MW-7	11/14/2013	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	4	**5**	**3**
MW-7	03/18/2014	<50	<29 a	<68 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	**2**	**3**
MW-7	05/28/2014	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	<0.5	**3**	**3**
MW-7	08/29/2014	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	**2**
MW-7	12/10/2014	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	<0.5	**2**	**3**
MW-7	03/13/2015	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	1	**5**	**3**
MW-8	08/31/2011	4,400	240	<67	<0.5	<0.7	41	442	**33**	--	--	--
MW-8	12/15/2011	8,100	96	<67	<0.5	<0.7	79	**880**	**72**	--	--	--
MW-8	02/06/2012	13,000	290	<69	<1	<1	110	**1,280**	**89**	--	--	--
MW-8	05/30/2012	9,500	700	<68	<1	<1	110	**1,300**	**96**	<2	<2 b	<2 b
MW-8 DUP	05/30/2012	10,000	450	<66	<1	<1	110	**1,300**	**93**	<2	<2 b	<2 b
MW-8	08/08/2012	9,300	290 a	<66 a	<1	<1	92	**850**	**73**	<2	<2 b	<2 b
MW-8 DUP	08/08/2012	11,000	240 a	<66 a	<1	<1	83	710	**67**	<2	<2 b	<2 b
MW-8	12/05/2012	13,000	2,600 a	200 a	<0.5	0.8	95	**1,100**	**93**	0.8	<1	<1 b
MW-8 DUP	12/05/2012	12,000	2,600 a	240 a	<0.5	0.8	91	**1,100**	**91**	0.8	<1	<1 b
MW-8	02/26/2013	12,000	780 a	<70 a	<0.5	0.6	100	**800**	**86**	<0.8	<1	<1 b
MW-8 DUP	02/26/2013	11,000	540 a	<69 a	<0.5	0.6	100	**770**	**72**	<0.8	<1	<1 b
MW-8	05/23/2013	6,800	380 a	<68 a	<0.5	<0.5	87	700	**86**	<0.8	<1	<1 b
MW-8 DUP	05/23/2013	7,000	380 a	<68 a	<0.5	0.5	100	**810**	**94**	<0.8	<1	<1 b
MW-8	08/29/2013	6,600	340 a	<66 a	<0.5	<0.5	60	450	**49**	<0.8	<1	<1 b
MW-8 DUP	08/30/2013	3,500	220 a	<66 a	<0.5	<0.5	47	350	**39**	<0.8	<1	<1 b
MW-8	11/14/2013	8,900	390 a	<67 a	<0.5	0.5	79	740	**67**	<0.8	<1	<1 b

Table B.1

Groundwater Data for Vapor Intrusion Screening
Former Tidewater Site
Phillips 66 Site 5173
Chevron Site 301233
2800 Martin Luther King Junior Way South
Seattle, Washington

		Petroleum Hydrocarbons Constituents								Chlorinated Solvents		
Location	**Date**	**TPHg**	**TPHd**	**TPHo**	**B**	**T**	**E**	**X**	**Naphthalene**	**PCE**	**TCE**	**VC**
MTCA Method B groundwater screening levels for vapor intrusion		**NE**	**NE**	**NE**	**2.4**	**15,600**	**2,780**	**310***	**8.93**	**22.9**	**1.55**	**0.347**
		µg/L	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**
MW-8 DUP	11/14/2013	8,000	320 a	<67 a	<0.5	0.6	81	**760**	**66**	<0.8	<1	<1 b
MW-8	03/19/2014	8,400	2,400 a	<67 a	<0.5	<0.5	33	370	**57**	1	<1	<1 b
MW-8 DUP	03/19/2014	8,800	2,200 a	110 a	<0.5	<0.5	42	480	**66**	1	<1	<1 b
MW-8	05/28/2014	5,600	860 a	<67 a	<0.5	<0.5	50	270	**39**	1	0.7	<0.5 b
MW-8 DUP	05/28/2014	5,900	910 a	<67 a	<0.5	<0.5	67	330	**59**	1	1	<0.5 b
MW-8	08/28/2014	11,000	500	<67	<0.5	0.8 J	170	590	**70**	<0.5	<0.5	<0.5 b
MW-8	12/10/2014	9,000	1,600	<66	<1	<1	94	350	**65**	<1	<1	<1 b
MW-8	03/12/2015	9,300	790	<66	<1	<1	92	390	**83**	<1	1 J	<1 b
MW-9	08/31/2011	<50	78	<68	<0.5	<0.7	<0.8	<0.8	<1	--	--	--
MW-9	12/15/2011	<50	<29	<67	<0.5	<0.7	<0.8	<1.6	<1	--	--	--
MW-9	02/06/2012	66	<300	<700 c	<0.5	<0.7	<0.8	<1.6	<1	--	--	--
MW-9	05/30/2012	66	<29	<67	<0.5	<0.7	<0.8	<0.8	<1	**120**	**130**	**9**
MW-9	08/08/2012	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	**100**	**130**	**8**
MW-9	12/05/2012	<50	39 a	<69 a	<0.5	<0.5	<0.5	<0.5	<1	**55**	**36**	**11**
MW-9	02/26/2013				Well Inaccessible				-	-	-	-
MW-9	05/24/2013	100	<29 a	<68 a	<0.5	<0.5	<0.5	<0.5	<1	**180**	**120**	**11**
MW-9	08/29/2013	<50	51 a	<66 a	<0.5	<0.5	<0.5	<0.5	<1	**65**	**43**	**7**
MW-9	11/13/2013	120	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	**150**	**120**	**8**
MW-9	03/18/2014	96	37 a	<66 a	<0.5	<0.5	<0.5	<0.5	<1	**180**	**100**	**13**
MW-9	05/27/2014	64	50 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	**140**	**120**	**14**
MW-9	08/28/2014	<50	44 J	<67	<0.5	<0.5	<0.5	<0.5	<1	**71**	**41**	**8**
MW-9	12/10/2014	81 J	56 J	<67	<0.5	<0.5	<0.5	<0.5	<1	**140**	**87**	**13**
MW-9	03/12/2015	60 J	86 J	<67	<0.5	<0.5	<0.5	<0.5	<1	**140**	**120**	**16**
MW-10	08/31/2011	<50	260	100	2	<0.7	<0.8	<0.8	<1	--	--	--
MW-10	12/15/2011	51	<28	<66	**3**	<0.7	<0.8	0.8	<1	--	--	--
MW-10	02/06/2012	<50 d	<29	<68	1	<0.7	<0.8	<1.6	<1	--	--	--
MW-10	05/30/2012	<50	74	<66	<0.5	<0.7	<0.8	<0.8	<1	<0.8	<1	**35**
MW-10 DUP	05/30/2012	-	-	-	-	-	-	-	-			
MW-10	08/07/2012	110	130 a	<68 a	1	<0.5	<0.5	1	<1	<0.8	<1	**36**
MW-10	12/06/2012	130	220 a	<72 a	**3**	0.6	<0.5	4	<1	<0.8	<1	**10**
MW-10	02/27/2013	<50	71 a	<69 a	0.8	<0.5	<0.5	<0.5	<1	<0.8	<1	**32**
MW-10	05/24/2013	<50	<29 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	<0.8	<1	**37**
MW-10	08/30/2013	<50	57 a	<66 a	0.8	<0.5	<0.5	1	<1	<0.8	<1	**41**
MW-10	11/13/2013	210	50 a	<67 a	2	<0.5	<0.5	3	<1	<0.8	<1	**30**
MW-10	03/18/2014	520	190 a	<66 a	2	0.7	<0.5	6	<1	<0.8	<1	**12**
MW-10	05/27/2014	<50	74 a	<67 a	<0.5	<0.5	<0.5	<0.5	<1	<0.5	0.6	**56**
MW-10	08/29/2014	<50	90 J	<67	<0.5	<0.5	<0.5	<0.5	<1	<0.5	0.6	**17**
MW-10	12/10/2014	140 J	140	<65	1	<0.5	<0.5	2	<1	<0.5	<0.5	**10**
MW-10	03/12/2015	99 J	100	<67	0.5 J	<0.5	<0.5	0.6 J	<1	<0.5	<0.5	**38**

Table B.1

Groundwater Data for Vapor Intrusion Screening
Former Tidewater Site
Phillips 66 Site 5173
Chevron Site 301233
2800 Martin Luther King Junior Way South
Seattle, Washington

		Petroleum Hydrocarbons Constituents								Chlorinated Solvents		
Location	**Date**	**TPHg**	**TPHd**	**TPHo**	**B**	**T**	**E**	**X**	**Naphthalene**	**PCE**	**TCE**	**VC**
MTCA Method B groundwater screening levels for vapor intrusion		**NE**	**NE**	**NE**	**2.4**	**15,600**	**2,780**	**310***	**8.93**	**22.9**	**1.55**	**0.347**
		µg/L	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**
MW-11	08/28/2014	580	<29	<67	<0.5	<0.5	<0.5	<0.5	<1	**1,200**	**38**	**0.6 J**
MW-11	12/10/2014	560	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	**1,200**	**37**	**0.6 J**
MW-11	03/12/2015	480	<29	<67	<0.5	<0.5	<0.5	<0.5	<1	**1,200**	**41**	**0.7 J**
MW-12	03/12/2015	--	--	--	--	--	--	--	--	--	--	--
MW-13	08/28/2014	<50	41 J	<66	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	**27**
MW-13	12/10/2014	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	1	<0.5	**26**
MW-13	03/12/2015	<50	<28	<66	<0.5	<0.5	<0.5	<0.5	<1	<0.5	<0.5	**26**

Notes
TOC = Top of casing
DTW = Depth to groundwater
GWE = Groundwater elevation
ft = Feet
ft-amsl = Feet above mean sea level
µg/L = Micrograms per liter
TPHg = Total petroleum hydrocarbons as gasoline range organics analyzed by NWTPH-Gx
TPHd = Total petroleum hydrocarbons as diesel range organices analyzed by NWTPH-Dx
TPHo = Total petroleum hydrocarbons as heavey oil range organices analyzed by NWTPH-Dx
VOCS = Volatile organic compounds
BTEX = Benzene, toluene, ethylbenzene, and xylenes analyzed by EPA Method 8260B; except the April 25, 1990 sample from EW-1 analyzed by EPA Method 8020
PCE = Tetrachloroethene analyzed by EPA Method 8260B
TCE = Trichloroethene analyzed by EPA Method 8260B
VC = Vinyl chloride analyzed by EPA Method 8260B
-- = Not analyzed
<x = Not detected above laboratory method detection limit.
NE = Not established
a = Analysis with Silica-gel Cleanup.
b = Analytes were not detected above the laboratory detection limits. However, the laboratory detection limits were above the MTCA Method A screening levels.
J = Estimated Value
[1] MTCA Method B groundwater screening levels are taken from Washington State Department of Ecology: 2015 Revised Groundwater, Sub-slab Soil gas, and Deep Soil Gas Screening Levels
http://www.ecy.wa.gov/programs/tcp/policies/VaporIntrusion/vig.html
Bolded concentrations indicate the concentration value exceeded the MTCA Method B screening levels
* = The xylenes screening level is lower of the two screening levels for m-xylenes (310 µg/L) and o-xylenes (440 µg/L)

Table B.2

Calculated Indoor Air Concentrations for Petroleum Hydrocarbon Constituents
Former Tidewater Site
Phillips 66 Site 5173
Chevron Site 301233
2800 Martin Luther King Junior Way South
Seattle, Washington

Well ID = MW-8 **Groundwater Depth = 10.56 (3/12/2015)**

	Groundwater Concentration a µg/L	*MTCA Method B Groundwater Screening Level [1] µg/L*	*Predicted Indoor Air Concentration µg/m3*	*MTCA Method B Air Cleanup Level [2] µg/m3*	*Groundwater to Indoor Air Attenuation Factor*	*Hazard Quotient*	*Risk Level*
B	<1	2.4	0.000361	0.32	6.24E-05	8.25E-06	5.05E-10
T	0.8	15,600	0.000675	2,290	6.59E-05	1.16E-06	--
E	170	2,780	0.147	457	6.20E-05	1.00E-04	--
X	590	750 b	0.244	45.7	4.51E-05	1.67E-03	--
Naphthalene	**70**	8.93	0.000281	0.0735	6.04E-06	6.41E-05	--
TPHg	11,000	NE	**3,490**	2,700 c	1.12E-04	--	--
TPHd	1,600	NE	**376**	140 d	1.03E-04	--	--

Well ID = MW-10 **Groundwater Depth = 10.29 (3/12/2015)**

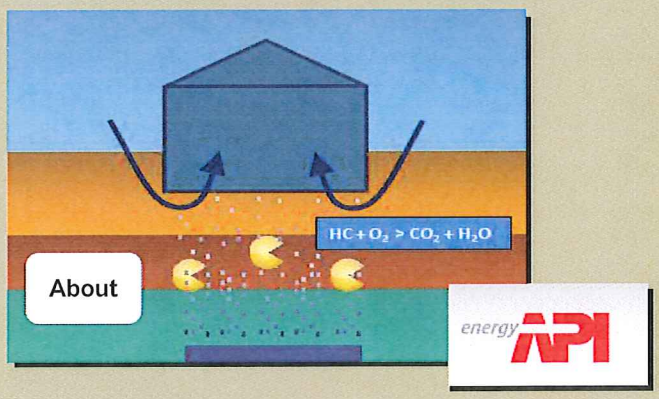
	Groundwater Concentration a µg/L	*MTCA Method B Groundwater Screening Level [1] µg/L*	*Predicted Indoor Air Concentration µg/m3*	*MTCA Method B Air Cleanup Level [2] µg/m3*	*Grooundwater to Indoor Air Attenuation Factor*	*Hazard Quotient*	*Risk Level*
B	1	2.4	0.0000426	0.32	3.68E-06	9.73E-07	5.96E-11
T	<0.5	15,600	0.0000135	2,290	4.21E-06	2.31E-08	--
E	<0.5	2,780	0.0000132	457	3.80E-06	9.05E-09	--
X	2	750 b	0.0000328	45.7	1.78E-06	2.24E-07	--
Naphthalene	<1	9	8.98E-10	0.0735	2.71E-09	2.05E-10	--
TPHg	140	NE	6.41	2,700 c	1.62E-05	--	--
TPHd	140	NE	4.02	140 d	1.26E-05	--	--

Notes:
MTCA = Model Toxics Control Act
Groundwater depths in feet below top of casing (BTOC).
<x = Not detected at laboratory reporting limit x
NE = Not established
Concentrations in bold type indicate the analyte was detected above MTCA Method B groundwater screening levels
TPHg = Total petroleum hydrocarbons as gasoline range organics analyzed by NWTPH-Gx
TPHd = Total petroleum hydrocarbons as diesel range organices analyzed by NWTPH-Dx
BTEX = Benzene, toluene, ethylbenzene, and xylenes analyzed by EPA Method 8260B
Naphthalene analyzed by EPA Method 8260B
[1] MTCA Method B groundwater screening levels are taken from Washington State Department of Ecology: 2015 Revised Groundwater, Sub-slab Soil gas, and Deep Soil Gas Screening Levels
http://www.ecy.wa.gov/programs/tcp/policies/VaporIntrusion/vig.html
[2] MTCA Method B indoor air cleanup levels for air phase hydrocarbons are taken from Table B-1. Indoor Air Cleanup Levels, Groundwater Screening Levels, and Soil Gas Screening Levels.
"Draft Guidance for Evaluating Soil Vapor Intrusion In Washington State: Investigation and Remedial Action", Department of Ecology, State of Washington, October 2009.
MTCA Method B Air Cleanup Levels for other constituents are taken from Washington State Department of Ecology: Cleanup Levels and Risk Calculation (CLARC) database
https://fortress.wa.gov/ecy/clarc/CLARCHome.aspx
Bolded concentrations indicate the concentration value exceeded the MTCA Method B screening levels
a = The hightest concentrations in the last four sampling events are used
b = The total xylenes screening level is calculated by adding up the screening levels for m-xylenes (310 µg/L) and o-xylenes (440 µg/L)
c = the cleanup levels is for aliphatic air phase hydrocarbon in C-5 through C-8 hydrocarbon range
c = the cleanup levels is for aliphatic air phase hydrocarbon in C-9 through C-12 hydrocarbon range

BioVapor

A 1-D vapor intrusion Model:

with Oxygen-Limited Aerobic Biodegradation



1) PROJECT INFORMATION

Site ID #:	Chevron 301233-MW-8
Address:	2800 MLK, Seattle, WA
Completed by:	JS
Date:	8-Jun-15
Job ID:	61992

BioVapor Version 2.0

2) INPUT SCREENS

1) Environmental

2) Chemicals

3) Chemical

Chemical

3) RESULTS SCREENS

1) VI Risk

2) Subsurface

3) Detailed

Site Name: Chevron 301233
Address: 2800 MLK, Seattle, WA

BioVapor Input

Date: 6/8/2015
Completed By: JS
Job ID: 61992

Model Input Screens: Environmental Factors | Chemicals | Chemical Concentrations | Chemical Database

1. Oxygen Surface Boundary Condition

Slab or Basement Foundation (e.g., Specify Airflow)

2. Indoor Target Criteria

- (●) Do not perform backward Calculation
- ( ) Based on Indoor Risk / Hazard Target
- ( ) Specified Indoor Air Concentration Target

Note: Target indoor air concentrations can be edited on the "Chemical Database" screen

3. Exposure and Risk Factors

Target Hazard Quotient For Individual Chemicals	THQ	1.00	(-)
Target Excess Individual Lifetime Cancer Risk	TR	1.00E-06	(-)
Carcinogen Averaging Time	AT_c	70.00	yrs
Non-carcinogenic Averaging Time	AT_{NC}	25.00	yrs
Body Weight - Adult	BW	70.00	kg
Exposure Duration	ED	25.00	yrs
Exposure Frequency	EF	250.00	days/yr
Indoor Inhalation Rate Exposure Adjustment	CF	1.00	(-)

4. Building Parameters

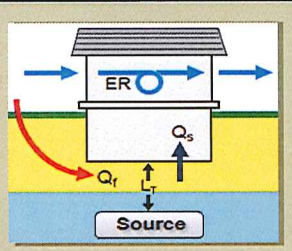
Indoor Mixing Height	L_{mix}	300.00	cm
Air Exchange Rate	ER	12.00	1/day
Foundation Thickness	L_{crack}	15.00	cm
Foundation Area	A_b	10083696.00	cm^2
Foundation Crack Fraction	η	3.77E-04	cm^2-cracks/cm^2-total
Total Porosity (Soil-filled Cracks)	$\theta_{T\text{-}crack}$	1.00	cm^3-void/cm^3-soil
Water Filled Porosity (Soil-filled Cracks)	$\theta_{w\text{-}crack}$	0.00	cm^3-void/cm^3-soil
Airflow Through Basement Foundation	Q_s	83.00	cm^3-air/sec
Building Envelope Resistance	L_{mix} * ER	0.04	cm/sec

5. Vadose Zone Parameters

Soil Porosity	$\theta_{T\text{-}soil}$	0.38	cm^3-void/cm^3-soil
Soil Water Content	$\theta_{w\text{-}soil}$	0.05	cm^3-water/cm^3-soil
Soil Organic Carbon Fraction	f_{oc}	5.00E-03	cm^3-void/cm^3-soil
Soil Density - Bulk	ρS	1.70	g-soil/cm^3-soil
Airflow Under Foundation	Q_f	83.00	cm^3-air/sec
Depth of Aerobic Zone Under Foundation	L_A	-	cm
O_2 Concentration Under Foundation	Co_2-e	-	%
Annual Median Soil Temperature	T	10.00	°C
Baseline Soil Oxygen Respiration Rate (Calculated from Foc)	Λ_{base}	9.780E-08	mg-O_2 / g-soil - sec
Depth to Source (from bottom of foundation)	LT	322.00	cm
Minimum O_2 Conc. For Aerobic Biodegradation		1.00	%

Legend

80.00	Calculated Value
80.00	User Input Value
80.00	Value Outside Normal Range



6. Commands and Options

Default Values

- ( ) Residential
- (●) Commercial / Industrial

Paste | Home | Print | Reset | Next

Site Name: Chevron 301233
Address: 2800 MLK, Seattle, WA

BioVapor Inputs

Date: 6/8/2015
Completed By: JS
Job ID: 61992

Model Input Screens: Environmental Factors | Chemicals | Chemical Concentrations | Chemical Database

2. Commands and Options

Home | Print | Previous | Next :: Results | ?

1. Ground Water Source Chemical Concentrations

Chemical	ug/L
benzene	5.00E-01
ethylbenzene	1.70E+02
toluene	8.00E-01
xylenes (mixed isomers)	5.90E+02
naphthalene	7.00E+01
TPH-GRO (C6-C10)	1.10E+04
TPH-DRO (>C10-C28)	1.60E+03

1.34E+04 Total Entered Hydrocarbon Concentration (ug/L)

Note: The total hydrocarbon concentration should equal the total concentration of all hydrocarbons in the source area

3. Attenuation Factor

0.1 Groundwater to Deep Soil Gas Attenuation Factor

Model Output Screens: VI Risk | Subsurface Profile | Detailed Results

Commands and Options: Home | Print | Previous | Next | Unprotect | ?

Target Hazard Quotient	Target Risk Level
1	1.00E-05

Forward Risk Calculation

Chemical Name	Groundwater Source Concentration	Soil Gas Source Concentration	Soil Gas to Indoor Air Attenuation Factor	Target Indoor Air Concentration	Predicted Indoor Air Concentration	Hazard Quotient	Risk Level
	ug/L	ug/m^3	(-)	ug/m^3-air	ug/m^3-air	(-)	(-)
benzene	5.00E-01	5.79E+00	6.24E-05	3.20E-01	3.61E-04	8.25E-06	5.05E-10
ethylbenzene	1.70E+02	2.36E+03	6.20E-05	4.60E+02	1.47E-01	1.00E-04	-
toluene	8.00E-01	1.03E+01	6.59E-05	2.20E+03	6.75E-04	1.16E-06	-
xylenes (mixed isomers)	5.90E+02	5.42E+03	4.51E-05	4.60E+01	2.44E-01	1.67E-03	-
naphthalene	7.00E+01	4.64E+01	6.04E-06	1.40E+00	2.81E-04	6.41E-05	-

NOTE A: "< 1E-100" means calculated attentuation factor is less than IE-100

Backward Risk Calculation

Critical Chemical for Backward Risk Calculation: Not Selected

Chemical Name	Target Hazard Quotient	Target Cancer Risk	Target Indoor Air Concentration	Soil Gas Source Concentration	Effective Saturated Vapor Concentration	Groundwater Source Concentration	Effective Solubility
	(-)	(-)	ug/m^3-air	ug/m^3	ug/m^3	ug/L	ug/L
benzene	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected
ethylbenzene	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected
toluene	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected
xylenes (mixed isomers)	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected
naphthalene	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected

NOTE B: Target indoor air concentrations can be edited on the "Chemical Database" screen
NOTE C: Red value indicates source concentration greater than saturation limit
NOTE D: Backward Risk Calculation not applicable when aerobic depth directly specified
NOTE E: Backward Calculation not completed due to Excel calculation error

Site Name: Chevron 301233
Address: 2800 MLK, Seattle, WA

BioVapor Results

Date: 6/8/2015
Completed By: JS
Job ID: 61992

Model Output Screens: VI Risk | Subsurface Profile | Detailed Results

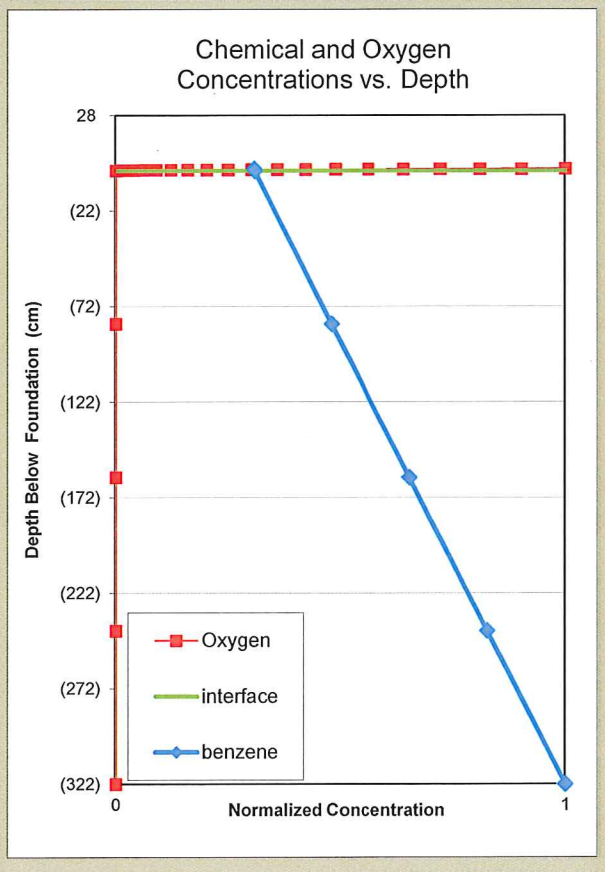
Commands and Options: Home | Print | Previous | Next | ?

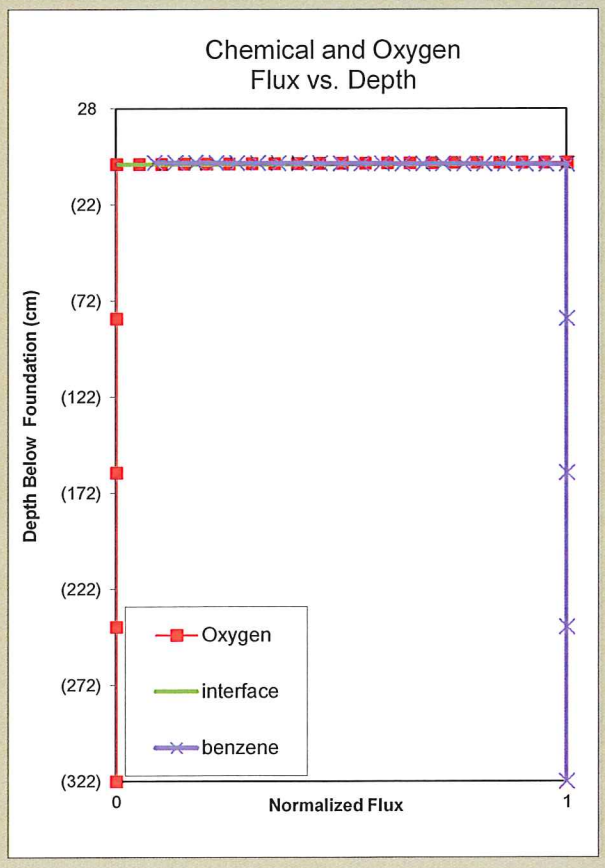
Select Chemical to View: benzene

Update Charts

Results Charts (Forward Calculation)

Predicted concentration profile below building foundation





Model Output Screens: VI Risk | Subsurface Profile | Detailed Results

Commands and Options: Home | Print | Previous | Unprotect | ?

General Results - Forward Calculations

Depth from building foundation to aerobic/anaerobic interface	Depth from aerobic/anaerobic interface to source	Total Depth
cm	cm	cm
0.89	321.11	322.00

Chemical Specific Results - Forward Calculations

Chemical	Foundation Mass Transfer Resistance	Soil Resistance	Sub-slab to indoor air attenuation factor	Aerobic/anaerobic interface to sub-slab attenuation factor	Source to aerobic/anaerobic interface attenuation factor	Source to indoor air attenuation factor	Source to indoor air attenuation factor (if no biodegradation)
	cm/sec	cm/sec	(-)	(-)	(-)	(-)	(-)
benzene	8.44E-06	4.42E-05	2.02E-04	9.97E-01	3.09E-01	6.24E-05	1.70E-04
ethylbenzene	8.34E-06	3.77E-05	2.00E-04	9.97E-01	3.11E-01	6.20E-05	1.64E-04
toluene	8.43E-06	4.37E-05	2.02E-04	9.97E-01	3.27E-01	6.59E-05	1.70E-04
xylenes (mixed isomers)	8.32E-06	3.58E-05	2.00E-04	9.95E-01	2.27E-01	4.51E-05	1.62E-04
naphthalene	8.26E-06	2.96E-05	1.98E-04	9.58E-01	3.18E-02	6.04E-06	1.55E-04
TPH-GRO (C6-C10)	8.56E-06	5.04E-05	2.05E-04	9.99E-01	5.47E-01	1.12E-04	1.75E-04
TPH-DRO (>C10-C28)	8.56E-06	5.02E-05	2.05E-04	9.98E-01	5.02E-01	1.03E-04	1.75E-04

BioVapor Results

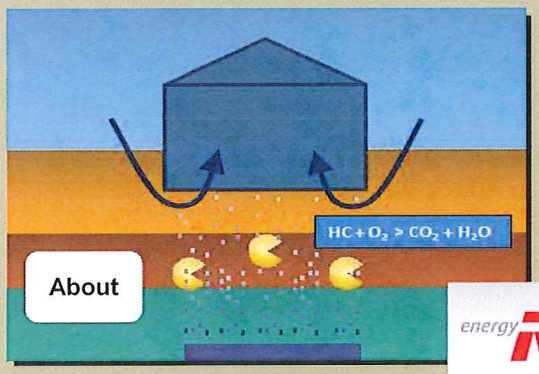
Chemical	Concentration in indoor air	Concentration in sub-slab gas	Concentration at aerobic/anaerobic interface	Concentration at source	Concentration in indoor air (if no biodegradation)	Flux into enclosure	Flux from source
	ug/m^3-air	ug/m^3-air	ug/m^3-air	ug/m^3-air	ug/m^3-air	ug/sec	ug/sec
benzene	3.61E-04	1.78E+00	1.79E+00	5.79E+00	9.84E-04	1.52E-04	1.8E-03
ethylbenzene	1.47E-01	7.32E+02	7.35E+02	2.36E+03	3.87E-01	6.16E-02	6.2E-01
toluene	6.75E-04	3.34E+00	3.35E+00	1.03E+01	1.74E-03	2.84E-04	3.0E-03
xylenes (mixed isomers)	2.44E-01	1.22E+03	1.23E+03	5.42E+03	8.78E-01	1.03E-01	1.5E+00
naphthalene	2.81E-04	1.41E+00	1.48E+00	4.64E+01	7.20E-03	1.18E-04	1.3E-02
TPH-GRO (C6-C10)	3.49E+03	1.70E+07	1.70E+07	3.11E+07	5.46E+03	1.47E+03	7.2E+03
TPH-DRO (>C10-C28)	3.76E+02	1.83E+06	1.84E+06	3.65E+06	6.41E+02	1.58E+02	9.2E+02
Totals	3.87E+03	1.88E+07	1.89E+07	3.48E+07	6.10E+03	1.62E+03	8.11E+03

Chemical	Oxygen Demand in Vadose Zone	Minimum O_2 Concentration at top of aerobic zone (i.e., below building foundation)	Oxygen mass flow at the top of aerobic zone
	% of total demand	%	ug/sec
benzene	0.00%		
ethylbenzene	0.01%		
toluene	0.00%		
xylenes (mixed isomers)	0.02%		
naphthalene	0.00%		
TPH-GRO (C6-C10)	81.79%		
TPH-DRO (>C10-C28)	11.68%		
Baseline Soil Oxygen Demand	6.50%		
Totals	100.00%	1.00%	2.29E+04

BioVapor

A 1-D vapor intrusion Model:

with Oxygen-Limited Aerobic Biodegradation



About

energy API

1) PROJECT INFORMATION

Site ID #:	Chevron 301233-MW10
Address:	2800 MLK, Seattle, WA
Completed by:	JS
Date:	8-Jun-15
Job ID:	61992

BioVapor Version 2.0

2) INPUT SCREENS

1) Environmental

2) Chemicals

3) Chemical

Chemical

3) RESULTS SCREENS

1) VI Risk

2) Subsurface

3) Detailed

Site Name: Chevron 301233-MW10
Address: 2800 MLK, Seattle, WA

BioVapor Input

Date: 6/8/2015
Completed By: JS
Job ID: 61992

Model Input Screens: Environmental Factors | Chemicals | Chemical Concentrations | Chemical Database

1. Oxygen Surface Boundary Condition

Slab or Basement Foundation (e.g., Specify Airflow)

2. Indoor Target Criteria

- (●) Do not perform backward Calculation
- ( ) Based on Indoor Risk / Hazard Target
- ( ) Specified Indoor Air Concentration Target

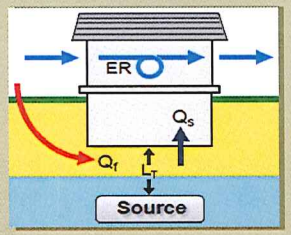
Note: Target indoor air concentrations can be edited on the "Chemical Database" screen

3. Exposure and Risk Factors

Target Hazard Quotient For Individual Chemicals	THQ	1.00	(-)
Target Excess Individual Lifetime Cancer Risk	TR	1.00E-06	(-)
Carcinogen Averaging Time	AT_c	70.00	yrs
Non-carcinogenic Averaging Time	AT_{NC}	25.00	yrs
Body Weight - Adult	BW	70.00	kg
Exposure Duration	ED	25.00	yrs
Exposure Frequency	EF	250.00	days/yr
Indoor Inhalation Rate Exposure Adjustment	CF	1.00	(-)

Legend

- 80.00 Calculated Value
- 80.00 User Input Value
- 80.00 Value Outside Normal Range



4. Building Parameters

Indoor Mixing Height	L_{mix}	300.00	cm
Air Exchange Rate	ER	12.00	1/day
Foundation Thickness	L_{crack}	15.00	cm
Foundation Area	A_b	5570000.00	cm^2
Foundation Crack Fraction	η	3.77E-04	cm^2-cracks/cm^2-total
Total Porosity (Soil-filled Cracks)	$\theta_{T\text{-}crack}$	1.00	cm^3-void/cm^3-soil
Water Filled Porosity (Soil-filled Cracks)	$\theta_{w\text{-}crack}$	0.00	cm^3-void/cm^3-soil
Airflow Through Basement Foundation	Q_s	83.00	cm^3-air/sec
Building Envelope Resistance	L_{mix} * ER	0.04	cm/sec

5. Vadose Zone Parameters

Soil Porosity	$\theta_{T\text{-}soil}$	0.38	cm^3-void/cm^3-soil
Soil Water Content	$\theta_{w\text{-}soil}$	0.05	cm^3-water/cm^3-soil
Soil Organic Carbon Fraction	f_{oc}	5.00E-03	cm^3-void/cm^3-soil
Soil Density - Bulk	ρs	1.70	g-soil/cm^3-soil
Airflow Under Foundation	Q_f	83.00	cm^3-air/sec
Depth of Aerobic Zone Under Foundation	L_A	-	cm
O_2 Concentration Under Foundation	Co_2-e	-	%
Annual Median Soil Temperature	T	10.00	°C
Baseline Soil Oxygen Respiration Rate (Calculated from Foc)	Λ_{base}	9.780E-08	mg-O_2 / g-soil - sec
Depth to Source (from bottom of foundation)	LT	314.00	cm
Minimum O_2 Conc. For Aerobic Biodegradation		1.00	%

6. Commands and Options

Default Values

- ( ) Residential
- (●) Commercial / Industrial

Paste | Home | Print | Reset | Next

Site Name: Chevron 301233-MW10
Address: 2800 MLK, Seattle, WA

BioVapor Inputs

Date: 6/8/2015
Completed By: JS
Job ID: 61992

Model Input Screens
Environmental Factors | Chemicals | Chemical Concentrations
Chemical Database

2. Commands and Options

Home | Print | Previous | Next :: Results | ?

1. Ground Water Source Chemical Concentrations

Chemical	ug/L
benzene	1.00E+00
ethylbenzene	2.50E-01
toluene	2.50E-01
xylenes (mixed isomers)	2.00E+00
naphthalene	5.00E-01
TPH-GRO (C6-C10)	1.40E+02
TPH-DRO (>C10-C28)	1.40E+02

2.84E+02 Total Entered Hydrocarbon Concentration (ug/L)

Note: The total hydrocarbon concentration should equal the total concentration of all hydrocarbons in the source area

3. Attenuation Factor

0.1 Groundwater to Deep Soil Gas Attenuation Factor

Model Output Screens: VI Risk | Subsurface Profile | Detailed Results

Commands and Options ?

Home | Print | Previous | Next | Unprotect

Target Hazard Quotient	Target Risk Level
1	1.00E-06

Forward Risk Calculation

Chemical Name	Groundwater Source Concentration	Soil Gas Source Concentration	Soil Gas to Indoor Air Attenuation Factor	Target Indoor Air Concentration	Predicted Indoor Air Concentration	Hazard Quotient	Risk Level
	ug/L	ug/m³	(-)	ug/m³-air	ug/m³-air	(-)	(-)
benzene	1.00E+00	1.16E+01	3.68E-06	3.20E-01	4.26E-05	9.73E-07	5.96E-11
ethylbenzene	2.50E-01	3.48E+00	3.80E-06	4.60E+02	1.32E-05	9.05E-09	-
toluene	2.50E-01	3.20E+00	4.21E-06	2.20E+03	1.35E-05	2.31E-08	-
xylenes (mixed isomers)	2.00E+00	1.84E+01	1.78E-06	4.60E+01	3.28E-05	2.24E-07	-
naphthalene	5.00E-01	3.32E-01	2.71E-09	1.40E+00	8.98E-10	2.05E-10	-

NOTE A: "< 1E-100" means calculated attentuation factor is less than IE-100

Backward Risk Calculation

Critical Chemical for Backward Risk Calculation: Not Selected

Chemical Name	Target Hazard Quotient	Target Cancer Risk	Target Indoor Air Concentration	Soil Gas Source Concentration	Effective Saturated Vapor Concentration	Groundwater Source Concentration	Effective Solubility
	(-)	(-)	ug/m³-air	ug/m³	ug/m³	ug/L	ug/L
benzene	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected
ethylbenzene	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected
toluene	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected
xylenes (mixed isomers)	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected
naphthalene	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected	Not Selected

NOTE B: Target indoor air concentrations can be edited on the "Chemical Database" screen

NOTE C: Red value indicates source concentration greater than saturation limit

NOTE D: Backward Risk Calculation not applicable when aerobic depth directly specified

NOTE E: Backward Calculation not completed due to Excel calculation error

Site Name: Chevron 301233-MW10
Address: 2800 MLK, Seattle, WA

BioVapor Results

Date: 6/8/2015
Completed By: JS
Job ID: 61992

Model Output Screens: VI Risk | Subsurface Profile | Detailed Results

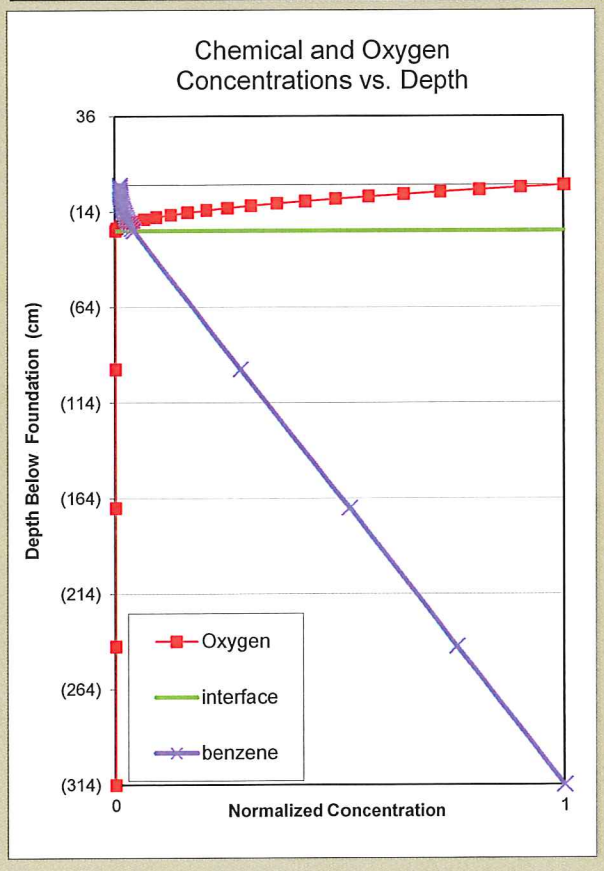
Commands and Options: Home | Print | Previous | Next | ?

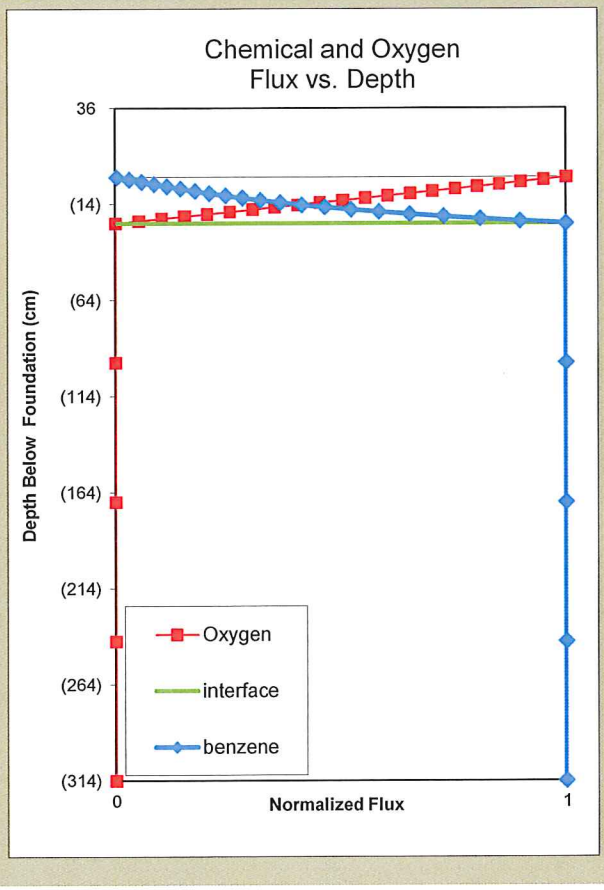
Select Chemical to View: benzene

Update Charts

Results Charts (Forward Calculation)

Predicted concentration profile below building foundation





Model Output Screens: VI Risk | Subsurface Profile | Detailed Results

Commands and Options: Home | Print | ? | Previous | Unprotect

General Results - Forward Calculations

Depth from building foundation to aerobic/anaerobic interface	Depth from aerobic/anaerobic interface to source	Total Depth
cm	cm	cm
23.95	290.05	314.00

Chemical Specific Results - Forward Calculations

Chemical	Foundation Mass Transfer Resistance	Soil Resistance	Sub-slab to indoor air attenuation factor	Aerobic/anaerobic interface to sub-slab attenuation factor	Source to aerobic/anaerobic interface attenuation factor	Source to indoor air attenuation factor	Source to indoor air attenuation factor (if no biodegradation)
	cm/sec	cm/sec	(-)	(-)	(-)	(-)	(-)
benzene	1.49E-05	4.53E-05	3.58E-04	2.55E-01	4.03E-02	3.68E-06	2.69E-04
ethylbenzene	1.49E-05	3.86E-05	3.58E-04	2.60E-01	4.08E-02	3.80E-06	2.58E-04
toluene	1.49E-05	4.48E-05	3.58E-04	2.78E-01	4.24E-02	4.21E-06	2.69E-04
xylenes (mixed isomers)	1.49E-05	3.68E-05	3.58E-04	1.56E-01	3.20E-02	1.78E-06	2.55E-04
naphthalene	1.49E-05	3.04E-05	3.58E-04	7.33E-04	1.03E-02	2.71E-09	2.40E-04
TPH-GRO (C6-C10)	1.49E-05	5.16E-05	3.59E-04	5.65E-01	7.98E-02	1.62E-05	2.78E-04
TPH-DRO (>C10-C28)	1.49E-05	5.15E-05	3.59E-04	5.06E-01	6.92E-02	1.26E-05	2.78E-04

BioVapor Results

Chemical	Concentration in indoor air	Concentration in sub-slab gas	Concentration at aerobic/anaerobic interface	Concentration at source	Concentration in indoor air (if no biodegradation)	Flux into enclosure	Flux from source
	ug/m^3-air	ug/m^3-air	ug/m^3-air	ug/m^3-air	ug/m^3-air	ug/sec	ug/sec
benzene	4.26E-05	1.19E-01	4.67E-01	1.16E+01	3.12E-03	9.89E-06	3.0E-03
ethylbenzene	1.32E-05	3.69E-02	1.42E-01	3.48E+00	8.97E-04	3.07E-06	7.8E-04
toluene	1.35E-05	3.77E-02	1.36E-01	3.20E+00	8.60E-04	3.13E-06	8.3E-04
xylenes (mixed isomers)	3.28E-05	9.16E-02	5.87E-01	1.84E+01	4.67E-03	7.60E-06	3.9E-03
naphthalene	8.98E-10	2.51E-06	3.43E-03	3.32E-01	7.96E-05	2.08E-10	6.0E-05
TPH-GRO (C6-C10)	6.41E+00	1.79E+04	3.16E+04	3.96E+05	1.10E+02	1.49E+00	1.1E+02
TPH-DRO (>C10-C28)	4.02E+00	1.12E+04	2.21E+04	3.20E+05	8.88E+01	9.32E-01	9.2E+01
Totals	1.04E+01	2.91E+04	5.38E+04	7.16E+05	1.99E+02	2.42E+00	2.06E+02

Chemical	Oxygen Demand in Vadose Zone	Minimum O_2 Concentration at top of aerobic zone (i.e., below building foundation)	Oxygen mass flow at the top of aerobic zone
	% of total demand	%	ug/sec
benzene	0.00%		
ethylbenzene	0.00%		
toluene	0.00%		
xylenes (mixed isomers)	0.00%		
naphthalene	0.00%		
TPH-GRO (C6-C10)	1.76%		
TPH-DRO (>C10-C28)	1.56%		
Baseline Soil Oxygen Demand	96.68%		
Totals	100.00%	1.13%	2.29E+04

Appendix C
Standard Operating Procedures for Vapor Intrusion Investigations

Soil Gas Sampling Standard Operating Procedures

Table of Contents

Figure Index

1. Soil Gas Sampling Standard Operating Procedures

1.1 Introduction

The procedures described in this section pertain to the installation of temporary and permanent soil gas and sub-slab probes to assess the vapor intrusion pathway. Soil gas and sub-slab probes are both used to collect soil gas samples; however, soil gas probes are installed at a greater depth, often outside a building, and sub-slab probes are installed to collect soil gas samples from immediately below a slab on grade or a basement floor slab. Permanent probes are recommended when more than one sampling event is required or when assessing seasonal variations in soil gas concentrations. Temporary probes are suitable for conducting a screening level assessment of vapor intrusion where the results could assist in locating future, permanent soil gas probes. Temporary probes are also suitable for conducting a preliminary evaluation of the magnitude and extent of volatile organic compound (VOC) impacts to the subsurface (e.g., such as in the case of a soil gas survey).

1.2 Prior Planning and Preparation

When designing and constructing soil gas and sub-slab probes the following questions should be considered:

1. What is the purpose of the soil gas probes?
2. What are the potential health and safety hazards?
3. What type(s) of soil gas probe construction materials are to be used?
4. What kinds of analyses are required (e.g., VOCs, petroleum hydrocarbon fractions)?
5. What are the geologic/hydrogeologic conditions at the site?
6. What are the seasonally high water table levels?
7. Is the water table shallow, (i.e., less than 1 metre below ground surface)?
8. Do perched conditions exist at the site?
9. What is the anticipated total depth of the probes?
10. Are nested soil gas probes required for vertical delineations?
11. Does a vapor barrier already exist under the slab, if so, sub-slab sampling might puncture the barrier, so the hole must be carefully resealed after monitoring is complete?
12. If a basement exists, could the primary entry point(s) for vapor intrusion be through the sidewalls rather than from below the floor slab? If so, sub-slab samples might need to be augmented with samples through the basement walls.
13. Although sample collection and analysis are analogous to those in other types of soil gas sampling, is an analytical method with lower detection limits required?

Note: If field staff are not aware of and able to answer all of the above noted questions before undertaking work in the field, the work plan must be reviewed in detail with the Project Coordinator/Manager. The project team may also consider involving GHD's vapor intrusion and human health risk assessment team during the initial planning to streamline the data evaluation.

1.3 Safety and Health

GHD is committed to conducting field activities with sound safety and health practices. GHD adheres to high safety standards to protect the safety and health of all employees, subcontractors, customers, and communities in which they work. The safety and health of our employees takes precedence over cost and schedule considerations.

Field personnel are required to implement the Safety Means Awareness Responsibility Teamwork (SMART) program as follows:

- Assure the Health and Safety Plan (HASP) is specific to the job and approved by a Regional Safety & Health Manager.
- Confirm that all HASP elements have been implemented for the job.
- A Job Safety Analysis (JSA) for each task has been reviewed, modified for the specific site conditions and communicated to all appropriate site personnel. The JSAs are a component of the HASP.
- Incorporate Stop Work Authority; Stop, Think, Act, Review (STAR) process; Safe Task Evaluation Process (STEP) Observations process; Near Loss and Incident Management process in the day-to-day operations of the job.
- Review and implement applicable sections of the GHD Safety & Health Policy Manual.
- Confirm that all site personnel have the required training and medical surveillance, as defined in the HASP.
- Be prepared for emergency situations, locating safety showers, fire protection equipment, evacuation route, rally point, and first aid equipment before you begin working, and make sure that the equipment is in good working order.
- Maintain all required Personal Protective Equipment (PPE), safety equipment, and instrumentation necessary to perform the work effectively, efficiently and safely.
- Be prepared to call the GHD Incident Hotline at 1-866-529-4886 for all incidents involving injury/illness, property damage, and vehicle incident and/or significant Near Loss.

It is the responsibility of the Project Manager to:

- Ensure that all GHD field personnel have received the appropriate health and safety and field training and are qualified to complete the work.
- Provide subcontractors with a Job Hazard Analysis to enable them to develop their own HASP.
- Ensure that all subcontractors meet GHD's (and the Client's) safety requirements.

1.4 Quality Assurance/Quality Control

Quality assurance and quality control procedures should be implemented in every step of the assessment process to ensure the collection of data of acceptable quality. A well-designed Quality Assurance/Quality Control (QA/QC) program will:

- Ensure that data of sufficient quality are obtained in order to facilitate an efficient site investigation.
- Allow for monitoring of staff and subcontractor performance.
- Verify the quality of the data.

The QA/QC program is developed on a site-specific basis.

1.5 Design Considerations

Diameter

Soil Gas Probes

The probe casing diameter should be kept to a minimum to reduce the volume of soil gas that must be purged from the probe during sampling. A maximum casing diameter of 3/4-inch (19 mm) to 1-inch (25 mm) will be used for solid piping casing material (e.g., polyvinyl chloride [PVC]), although casing diameters this large are not recommended for deep soil gas probes (e.g., greater than 15 feet [4.6 m]) since large purge volumes (e.g., milliliters) will result. Casing diameters of 1/4 inch (6.4 mm) to 3/8-inch (9.5 mm) are typical when flexible tubing is used for the casing material (e.g., Teflon or nylon).

Sub-Slab Probes

A typical sub-slab probe is constructed from small-diameter (e.g., 01/8- or 1/4-inch outside diameter) stainless steel or another inert material and stainless steel compression fittings. The probes are cut at a length to either float in the slab, if appropriate for your site conditions, or to extend to the base of the slab.

Screened Interval and Sand Pack Material

Soil Gas Probes

The length and depth of the perforated (screened) section should consider the desired monitoring interval as well as the geologic conditions encountered. A typical screened section would consist of a 6-inch (0.15 m) to 1-foot (0.3 m) perforated section. The use of prefabricated stainless steel screen implants is common. Alternatively, the screened interval can be created from casing material by hand-cutting slots, or hand-drilling holes, into the casing at a regular pattern. For hand-cut or hand-drilled screened intervals, the preferred sand pack material for soil gas probes is pea gravel. For prefabricated screens, the preferred sand pack material is inert 10/20 silica sand (#1 morie sand) or glass beads.

Sub-Slab Probes

A screen is not always used with sub-slab probes. When a screen is utilized, it is often pre-fabricated with a length of approximately 6 inches, due to the limited depth intervals sampled. When a screen is not utilized, the bottom of the probe is left open to facilitate sample collection. The perforated or open section should be consistent with the desired monitoring interval and sub-slab conditions encountered.

Monitoring Parts

For both soil gas and sub-slab probes, airtight stainless steel or brass compression fittings (e.g., Swagelok) with valves should be installed at ground surface to allow for an airtight connection to sampling equipment. The valve is required to isolate the soil gas sampling assembly from the soil gas probe while sampling assembly airtightness tests are conducted prior to probe purging and sampling.

Casing Materials

Soil Gas Probes

The materials selected for soil gas probe casing construction must be compatible with the volatile chemicals anticipated to be present in soil gas. Experience has shown that PVC casing is suitable when VOCs are present. However, as described above, PVC is typically not available in small enough diameters to provide practical soil gas probe purge volumes. To minimize purge volumes, small diameter (e.g., 1/4-inch [6.4 mm] to 3/8-inch [9.5 mm]) flexible tubing (e.g., Teflon or nylon) is more commonly applied as the soil gas probe casing. Where solid casing is used (i.e., PVC), threaded piping will be used to avoid any possible contamination from solvent cement.

Sub-Slab Probes

The materials selected for sub-slab casing construction must be compatible with the volatile chemicals anticipated to be present in soil gas. Often, 1/4-inch OD stainless steel tubing is utilized to collect sub-slab soil gas. The length of the stainless steel (or brass) tubing is cut to a desired length prior to installation.

1.6 Soil Gas and Sub-Slab Probe Installation

The information contained in this section has been compiled from existing manuals, various reference documents, and a broad range of colleagues with considerable practical and educational backgrounds. This SOP outlines the generic procedures necessary to install a soil gas/sub-slab probe. Site conditions, contaminants and geology may require modification of this procedure. Review applicable government procedures and informational documentation prior to installation.

This SOP is not intended to prohibit those conducting evaluations from using means other than those specified herein to measure soil gas concentrations; however, departures from this guidance will often need to include information for a more detailed review.

1.6.1 Installation Procedures - Soil Gas Probes

The soil gas probe is to be installed using Geoprobe® dual tube sampling system to advance a borehole to the target depth. The dual-tube sampling system consists of first advancing a 2 1/2-inch (6.4 cm) diameter inner sampling probe followed by advancing a 3 1/2-inch (8.9 cm) diameter outer casing. The outer casing should cut away disturbed soil immediately surrounding the borehole left by the inner probe. The outer casing should create a zone of reduced soil disturbance due to the inner probe having already been advanced. It is anticipated that using the dual tube system will result in a minimum amount of soil disturbance around the borehole annulus. The soil lithology should be logged during drilling activities and recorded on a field boring log along with any applicable observations. Permanent soil vapor probes can be installed with a conventional drill rig equipped with a hollow-stem auger, although increased formation disturbances would likely result. Rotosonic and mud or air rotary drilling methods are not recommended since they can influence soil vapor sample results and/or alter the physical properties of the subsurface adjacent to the borehole annulus.

The probes should be constructed with a 6-inch (15 cm) to 12-inch (30 cm) long screened interval. The screened interval can be hand-fabricated or prefabricated. The probe casing should be constructed using flexible tubing or solid casing. Flexible tubing (e.g., Teflon or nylon) of small diameter (e.g., 1/4-inch [6.4 mm] to 3/8-inch [9.5 mm]) is most commonly used in combination with prefabricated screened intervals. Solid casing (e.g., PVC) of small diameter (e.g., 3/4-inch [19 mm] to 1-inch [25 mm]) is most commonly used with hand-fabricated screened intervals. After positioning the screened interval and casing into the borehole, the screen should be surrounded by the appropriate sand pack material (i.e., pea gravel for hand-fabricated screens and 10/20 silica sand for prefabricated screens). When placing the sand pack into the borehole, 1 inch (2.5 cm) of sand pack material should be placed under the bottom of the probe screen to provide a firm footing. The sand pack should extend to 6 inches (15 cm) above the screened interval. A bentonite pellet seal should then be installed to 1-foot (0.3 m) above the sand pack and should be hand-hydrated. For temporary probes (i.e., that will be sampled for less than a year), the remaining annulus should be backfilled with pre-hydrated bentonite cement. For permanent probes (i.e., that will be sampled for more than a year), the remaining annulus should be backfilled with neat-cement grout[1] (Cal EPA, 2015). The soil gas probe casing should extend to ground surface and should be fitted with airtight stainless steel or brass compression fittings (e.g., Swagelok) with valves to allow for an airtight connection to soil gas sampling equipment. A flush-mount protective cover should be installed above the soil probe and cemented into place. Schematics of typical soil gas probe installation details are presented on Figures 15.1 and 15.2, respectively, where hand-fabricated and prefabricated screened intervals are applied.

1.6.2 Installation Procedures - Sub-Slab Soil Gas Probes

Sub-slab soil gas probes allow for collection of soil gas samples from directly beneath the slab of a building. Sub-slab soil gas probes are not recommended when groundwater is present directly below the slab, since the sub-slab port could allow groundwater to enter the building. Sub-slab soil

[1] Neat-Cement Grout means a mixture in the proportion of 94 pounds of Portland cement and not more than 6 gallons (22.7 liters) of water. Bentonite up to 5 percent by weight of cement (4.7 pounds of bentonite per 94 pounds of Portland cement) may be used to reduce shrinkage.

gas probes can be installed using several different methods: (1) utilizing a small diameter hole, (2) a larger diameter hole w/ flushmount casing, and (3) a Vapor Pin™. Summaries of the steps involved are presented below:

Small Diameter Sub-Slab Soil Gas Probe:

A schematic of a typical small diameter sub-slab soil gas probe installation detail is presented on Figure 15.3.

1. Prior to drilling holes in a foundation or slab, contact local utility companies to identify and mark utilities coming into the building from the outside (e.g., gas, water, sewer, refrigerant, and electrical lines). Consult with a local electrician and plumber to identify the location of utilities inside the building.
2. Prior to fabrication of the sub-slab vapor probes, use the rotary drill and the two inch diameter drill bit to create a shallow (e.g., 1/4 to 1/2 inch in depth) outer hole that partially penetrates the slab. This outer hole will allow the protective cap to be flush with the concrete surface (Figure 15.4).
3. Use a small portable vacuum cleaner to remove cuttings from the hole.
4. Use the rotary hammer drill and a one-inch drill bit to create a smaller diameter "inner" hole through the remainder of the slab to some depth (e.g., seven to eight centimeters or three inches) into the sub-slab material. Figure 15.5 illustrates the appearance of "inner" and "outer" holes. Drilling into the sub-slab material will create an open cavity, which will prevent the obstruction of any probes during sampling.
5. Use a small portable vacuum cleaner to remove cuttings from the hole.
6. Determine the thickness of the slab and record the measurement.
7. Assemble the vapor point using the basic design of a sub-slab vapor probe illustrated on Figure 15.3.
8. Place the assembled vapor point (Figure 15.6) into the hole and ensure the screen extends beyond the concrete and that the top of the probe is flush with the slab. Also apply the tamper resistant cap so as to not interfere with day-to-day use of the buildings. Cut tubing if necessary (Figure 15.7).
9. Confirm the fit of the rubber shaft plug to the sides of the boring. It should be snug with no gaps present. If additional thickness (diameter) is necessary, non-VOC plumbers putty can be added around the rubber.
10. Mix a quick-drying Portland cement to ensure a tight seal.
11. Inject the Portland cement with a 50 cc syringe or push into the annular space between the probe and outside of the "outer" hole (Figure 15.8).
12. Complete installed vapor point (Figure 15.9) with a plug (Figure 15.10) or tamper-resistant cap (Figure 15.11).
13. Allow cement to cure for at least 24 hours prior to sampling.

Sub-slab probes constructed in the aforementioned manner may be abandoned by removing any tubing and all surface protective covers. The boring annulus can then be backfilled with uncontaminated native material or grout. Inspect/clean the work area, and return site conditions to their original state.

If the tubing cannot be removed, the tubing should be cemented in place. All surface protective covers must be removed and returned to as close as possible to original site conditions.

Larger Diameter Hole w/ Flushmount Casing:

A schematic of a typical large diameter sub-slab soil gas probe installation detail is presented on Figure 15.12.

1. Prior to drilling holes into the building floor, the location of utilities coming into the building (e.g., gas, electrical, water, and sewer lines, etc.) must be identified. Avoid installing sub-slab soil gas probes near where utilities penetrate the slab as these may be entry points for downward ambient air migration through the slab during soil gas sampling.
2. A concrete corer is used to drill a hole through the concrete floor slab. The diameter of the hole should be sufficient to allow the installation of a protective casing within the hole. A sufficient space for placement of cement is required between the outer edge of the flush-mount casing and the hole in the concrete. Smaller diameter flush-mount protective casings are not recommended as they make accessing the probe within the casing difficult.
3. Once the hole in the concrete is cored and the center core removed, the flush-mount protective casing shroud should be cut to a suitable length. Ideally, the length of the shroud should allow the flush-mount casing to be flush with the surrounding floor while resting on the bedding material beneath the slab.
4. The probe assembly, including a valve at the top of the probe, should be placed so that the tip of the probe is within the bedding material beneath the concrete slab. Care should be taken to not force the probe into the bedding so that the open end of the probe doesn't plug. Note: the probe assembly should be vacuum-tested on both sides of the valve prior to installation. A piece of ¼ inch Teflon tubing should be attached at the top of the valve prior to installation. This tubing will allow easier access for the use of compression fittings to attach purging and sampling equipment to the probe.
5. The probe should be cemented into the flush-mount casing with hydraulic cement. The hydraulic cement should form a continuous seal from the bedding material to just below the top hex nut of the probe assembly.

Vapor Pin™

This SOP describes the procedure for installing a sub-slab soil probe using a Vapor Pin™. Borings should be done through the use of a rotary hammer drill. The specific drill utilized must be capable of utilizing the drill and coring bits identified by the SOP (see below) and be of sufficient size to penetrate the expected thickness of the concrete present.

General List of Materials

This installation SOP utilizes the following products, which are available from Cox-Colvin & Associates, Inc. Equipment:

1. Silicone sleeve.
2. Hammer drill.
3. 5/8 inch diameter hammer bit (Hilti™ TEYX 5/8" x 22" #00206514 or equivalent).
4. 1½ inch diameter hammer bit (Hilti™ TEYX 1½" x 23" #00293032 or equivalent) for flush mount applications.
5. 3/4 inch diameter bottle brush.
6. Wet/dry vacuum with HEPA filter (optional).
7. Vapor Pin™ installation/extraction tool.
8. Dead blow hammer.
9. Vapor Pin™ flush mount cover, as necessary.
10. Vapor Pin™ protective cap.
11. Equipment needed for abandonment.
12. Vapor Pin™ installation/extraction tool.
13. Dead blow hammer.
14. Volatile organic compound-free hole patching material (hydraulic cement) and putty knife or trowel.

Flushmount Vapor Pin™ Installation Protocol

1. Prior to drilling holes in a foundation or slab, contact local utility companies to identify and mark utilities coming into the building from the outside (e.g., gas, water, sewer, refrigerant, and electrical lines). Consult with a local electrician and plumber to identify the location of utilities inside the building.
2. Set up wet/dry vacuum to collect drill cuttings.
3. Drill a 1½ inch diameter hole at least 1¾ inches into the slab.
4. Remove the drill bit, brush the hole with the bottle brush, and remove the loose cuttings with the vacuum.
5. Drill a 5/8 inch diameter hole through the slab and at least six inches into the underlying soil to form a void.
6. Remove the drill bit, brush the hole with the bottle brush, and remove the loose cuttings with the vacuum.
7. Assemble the Vapor Pin™ assembly (Figure 15.13) by threading the Vapor Pin™ into the extraction/installation tool and placing the silicone sleeve over the barbed end.

8. Place the lower end of the Vapor Pin™ assembly into the drilled hole. Place the small hole located in the handle of the extraction/installation tool over the Vapor Pin™ to protect the barb fitting and cap, and tap the Vapor Pin™ into place using a dead blow hammer (Figure 15.14). Make sure the extraction/installation tool is aligned parallel to the Vapor Pin™ to avoid damaging the barb fitting.
9. Unscrew the threaded coupling from the installation/extraction handle and use the hole in the end of the tool to assist with the installation (Figure 15.15). During installation, the silicone sleeve will form a slight bulge between the slab and the Vapor Pin™ shoulder.
10. Place the protective cap on the Vapor Pin™ (Figure 15.16).
11. Cover the Vapor Pin™ with a flushmount cover.
12. Allow 20 minutes or more (consult applicable guidance for your situation) for the sub-slab soil gas conditions to equilibrate prior to sampling.
13. Remove protective cap and connect sample tubing to the barb fitting of the Vapor Pin™.

Temporary Soil Gas Probes

First, a core drill should be used to remove any surface cover, as needed. The temporary soil gas probes should consist of a decontaminated hollow sampling rod driven to the target depth below ground surface. The sampling rod should consist of a decontaminated 1-inch (2.5 cm) hollow stainless steel outer rod that is retracted to expose a 1-foot (0.3 m) long stainless steel screen. The rod should be advanced by a slide hammer to the target depth, and the outer rod retracted to expose the screen at the bottom of the rod. A surface seal comprised of hydrated bentonite cement should be placed around the base of the driven rod. The sampling rod should be completed at ground surface with airtight stainless steel or brass compression fittings (e.g., Swagelok) with valves to allow for an airtight connection to soil gas sampling equipment. A schematic of a typical temporary soil gas probe installation detail is presented on Figure 15.17.

1.6.3 Installation Documentation

Details of each soil gas probe installation should be recorded on GHD's standard Stratigraphic Log Overburden (Form SP-14), or recorded within a standard GHD field book. The Well Instrumentation Log (Form SP-15) is provided for recording the overburden well instrumentation details, and can be used for soil gas probe installations. This figure must note:

- Borehole depth
- Probe perforation intervals
- Filter pack intervals
- Plug intervals
- Grout interval
- Surface cap detail
- Soil gas probe material
- Soil gas probe instrumentation (i.e., riser and screen length)

- Soil gas probe diameter
- Filter pack material
- Backfill material detail
- Stickup/flush-mount detail
- Date installed

The soil stratigraphy encountered at soil gas probes refusal must be recorded in accordance with GHD's standard borehole advancement methods (see Section 5.0).

Each soil gas probe should be accurately located on a site sketch. An accurate field tie to the center of the gas probe from three adjacent permanent features should be completed. The field ties should be located in a different direction from the installation.

Each soil gas probe must be permanently marked to identify the soil gas probe number designation.

1.6.4 Follow-Up Activities

Once the soil gas probe(s) have been completed, the following activities need to be performed:

1. Conduct initial monitoring round of gas probes.
2. Submit all logs to the appropriate GHD hydrogeology department, who will be responsible for the generation of the final well log.
3. Survey accurate horizontal and vertical control of the soil gas borings and any pertinent structures needed to create a suitable site map.
4. Prepare an accurate soil gas probe/boring location map. Tabulate soil gas probe construction details.
5. Write-up all field activities including, but not necessarily limited to; drilling method(s), construction material, site geology.
6. Distribute all/any field book(s) to the appropriate GHD office.

1.7 Soil Gas and Sub-Slab Sampling Protocol

The following sampling protocols are for collecting a vapor sample through either a soil gas probe and/or sub-slab probe for the analysis of volatile organic compounds (VOCs) by the United States Environmental Protection Agency Method TO-15 (USEPA, 1999).

This SOP does not cover, nor is it intended to provide, a justification or rationale for where a sampling point is installed. It is assumed by using this SOP that site conditions have been fully evaluated and that the sampling location and depth meet the objectives outlined in the work plan or scope of work. Considerations must be given to the types of chemicals of concern, lithology encountered, and the depth of the vapor source. Samples collected deeper than any potential source of vapors may not fully characterize the potential risk and sampling points should never be installed or collected within the zone of saturation. The bottom of the probe should be approximately 0.5 m (1.6 ft) to 1 m (3.2 ft) above the highest water table.

Where possible, external probes should be installed at a minimum depth of 1 m (3.2 ft) to reduce the likelihood of ambient air being drawn through surficial soils (referred to as "short-circuiting"). External shallow probes less than 1 m (3.2 ft) deep may be warranted where there is a shallow water table. Good practice is to place a plastic sheet/tarp around a shallow probe to minimize atmospheric air intrusion (CCME, 2016). Recommended minimum dimensions of the plastic sheet/tarp are 1.5 m (5 ft) by 1.5 m (5 ft). The plastic/tarp should be weighted down at the edges with sand or sand bags (CCME, 2016).

Most soil gas/sub-slab probes are installed at relatively shallow depths (less than ten feet below ground surface) so minimum purge volumes and low-volume samples must be performed to minimize potential breakthrough from the surface or between sampling intervals. Tracer/leak gas is necessary to ensure breakthrough does not occur and that a leak does not occur at any fitting above grade. Sampling should not occur during a significant rain event. A significant rain event is defined as 0.5 inches or greater of rainfall during a 24-hour period by Cal EPA (2015), or 1 centimeter or greater of rainfall during a 24-hour period by MOE (2013). A period of 1 day for coarse-grained soil conditions and several days for fine-grained soil conditions after a significant rain event should occur prior to collecting soil vapor samples. This time interval is required for drainage to occur and soil conditions to return to ambient moisture conditions.

Note: The sampling interval after a significant event should be verified based on the applicable jurisdictional regulatory vapor intrusion guidance.

Samples from wells with multiple points installed must not be collected simultaneously and approximately 30 minutes must elapse between each sampled interval. Sample times should be documented on the field log. Sample flow rates are not to exceed 200 milliliters per minute (mL/min) to minimize the potential for vacuum extraction of contaminants from the soil phase. A flow rate greater than 200 mL/min may be used when purging times are excessive, such as for deep wells with larger-diameter tubing. However, a vacuum of 100 inches of water (7.4 inches of mercury [Hg]) or less must be maintained during sampling whenever a higher flow rate is used. Volumes of various tubing sizes are provided in Table 1 in order to aid in calculating purge volumes.

Table 1 Volumes for Select Tubing Sizes

Tubing Size (inches ID)	Volume/ft (liters)
3/16	0.005
¼	0.010
½	0.039

Care must be used during all aspects of sample collection to ensure that sampling error is minimized and high quality data are obtained. Care must also be taken to avoid excessive purging prior to sample collection and prevent pressure build-up in the enclosure during introduction of the tracer gas. Inspection of the installed sample probe, specifically noting the integrity of the surface seal and the porosity of the soil in which the probe is installed, will help to determine the tracer gas setup. The sampling team must avoid actions (e.g., fueling vehicles, using permanent marking pens, and wearing freshly dry-cleaned clothing or personal fragrances) which could potentially

cause sample interference in the field. All data collected should be recorded on the Sub-Slab/Soil Gas Sampling Field Data Sheet (SP-30).

1.7.1 Soil Gas Collection General List of Materials

The equipment required for soil gas sample collection is as follows:

Flow Meters and Detectors

1. Flow regulator with vacuum gauge. Flow regulators provided by a qualified laboratory are pre-calibrated to a specified flow rate (e.g., 100 mL/min).
2. Photoionization detector (with appropriate lamp).
3. Helium detector (if helium is utilized as a tracer gas).
4. Methane meter for petroleum sites that is capable of also measuring percent of methane (CH4), carbon dioxide (CO2), and oxygen (O2).
5. Low flow air pump (e.g., 100 mL/min) (as appropriate)

Tooling and Supplies

1. Sampling canister, Tedlar bag, or syringe (one per location).
2. Regulated flow meter assembly set to a maximum of 200 mL/min (one per location, as appropriate).
3. 1/4 inch tubing (Teflon®, polyethylene, or similar) and assorted fittings.
4. Plastic housing for using tracer gas.
5. 50 ml syringe (for purging).
6. Camera.
7. Adjustable crescent wrenches, small to medium size, and/or open end combo wrenches 9/16 to 1/2 inch.
8. Scissors/snips to cut tubing.
9. Ballpoint pens.
10. Nitrile gloves.
11. Compound to be used as tracer gas - lab grade helium or isopropyl alcohol (IPA).
12. Tarp or plastic sheeting

1.7.2 Soil Gas Tracer Compounds

A leak in the sampling assembly may allow ambient air into the system and dilute the soil gas results (Benton and Shafer, 2007). Therefore, tracer gases must be utilized during the collection of soil gas samples to verify that the sample collected is from the installed sampling point. The presence of a tracer compound, whether liquid or gaseous, can confirm a leak in the sampling train assembly and whether the usability of the sample will need to undergo further evaluation.

Careful thought and consideration must be used when choosing a leak check compound as a tracer, since each compound can have specific benefits and drawbacks.

Helium used as a tracer gas beneath a shroud allows for the screening of the sampling train in the field. In conjunction with the use of a field meter capable of detecting helium, leaks within the sampling train could be detected prior to sampling. A retightening of all fittings prior to collecting the sample for analysis should be done. If a leak has been detected and is unable to be resolved, the sampling point may need to be decommissioned and a new one installed. Only lab-grade helium (UHP-Ultra High Purity) should be used as a tracer, since helium available at general merchandise stores may contain secondary contaminants, such as benzene.

Understanding the relationship between a leak and the concentration detected of the tracer gas used to check for leaks, the potential for absorption of the tracer gas (i.e., helium) onto sample train tubing, and the potential for interference by the tracer gas compound with VOCs is important in answering the data usability. An ambient air leak of up to five percent may be acceptable if quantitative tracer testing is performed. A soil gas vapor well should be decommissioned if the leak cannot be corrected. Any replacement vapor wells should be installed at least five feet from the location where the original vapor well was located

Note: The ambient air leak of up to five percent leak should be verified based on the applicable jurisdictional regulatory vapor intrusion guidance.

1.7.3 Soil Gas and Sub-Slab Probe Leak Testing

The use of leak testing is recommended as a quality control check to ensure ambient air has not leaked into the soil gas probe or sampling assembly, which may affect (i.e., dilute) the analytical results. Contaminants in ambient air can also enter the sampling system and be detected in a sample from a non-contaminated sampling probe resulting in a "false positive" result. The leak testing should be conducted as described in the following two steps:

- Step 1 - Vacuum Test: used to ensure that the tubing and fittings/valves that make up the sampling assembly are air-tight
- Step 2 - Tracer Test: used to ensure that ambient air during soil gas sample collection is not drawn down the soil gas probe annulus through an incomplete seal between the formation and the soil gas probe casing.

The vacuum test and tracer test are detailed below.

Step 1 - Vacuum (shut-in) Test

- The sampling assembly must be connected to the soil gas probe valve at the surface casing. Once connected, the sampling assembly will consist of the soil gas probe, the vacuum gauge supplied by the laboratory, personal sampling pump, and Summa canister, all connected in series (i.e., in the order of soil gas probe, vacuum gauge, pump, and canister), using tee-connectors or tee-valves.
- The personal sampling pump will be used to conduct the vacuum test. The vacuum test should consist of opening the valve to the personal sampling pump while leaving closed the valves to

the Summa™ canister and the soil gas probe. The pump should then be operated to ensure that it draws no air from the sampling assembly (i.e., creates a negative pressure, or vacuum within the sampling assembly), thus establishing that all assembly connections are air-tight. The sampling pump low-flow detect switch will likely activate within 10 to 15 seconds, turning the pump off. A negative pressure, or vacuum, should be established within the sampling assembly, and should be sustained for at least 1 minute.

- If the pump is capable of drawing flow, or if the vacuum is not sustained for at least 1 minute, all fittings and tubing will be checked for tightness (or replaced) and the vacuum test will be repeated.
- The reading from the vacuum gauge pressure should be recorded in field logbook to demonstrate that the pump is able to create a vacuum within the sampling assembly (it will also be noted whether the low-flow detect switch on the pump was activated), and that the vacuum is sustained for at least 1 minute.

Step 2 - Tracer Test

A tracer compound is released at ground surface immediately around the soil gas probe surface casing and is used to test for ambient air leakage down the annulus of the soil gas probe and into the soil gas sample. Two options are described below for the tracer test where either isopropanol (Option A) or helium (Option B) is used as the tracer compound.

Option A - Isopropanol

- For Option A, isopropanol is used as the tracer compound. It is included as an analyte in U.S. EPA's TO-15 method, it is readily available (i.e., as isopropyl rubbing alcohol), and it is safe to use.
- Approximately 1 teaspoon (approximately 4 mL) of isopropanol (rubbing alcohol) should be mixed in 1 gallon of de-ionized water to create an approximate 1/1,000 solution.
- Paper towels soaked in a dilute solution of isopropanol should then be wrapped around the soil gas probe surface casing and ground surface immediately surrounding the surface casing. Soil gas probe surface casing then should be covered over, using clear plastic sheeting that will be sealed to the ground surface. As the ground surface finish permits, sealing the plastic sheeting to ground surface should be accomplished by using tape or by weighting the edges of the plastic sheeting with dry bentonite.
- Immediately before conducting the soil gas probe purging, remove the paper towels from the solution, wringing out the towels so they are very damp, but not dripping. Place them around the vapor probe and seal them in place using the plastic sheeting.
- The isopropanol solution should be kept fresh, with new solution being made every hour. The solution should be mixed at a central location away from the sampling activities. The isopropanol should be kept tightly capped and kept away from all sampling equipment. The solution should be kept away from the sampling assembly until immediately before sample collection begins. Sampling personnel must wear latex gloves while handling the solution and soaked paper towels, and will remove the gloves while working with the sampling assembly.

- Soil gas samples with laboratory analytical results for isopropanol that are greater than 10 percent of the starting concentration of isopropanol in the vapors emitted from dilute isopropanol solution should not be considered reliable and representative of soil gas concentrations within the formation (ITRC, 2007). The starting concentration should be calculated based on the concentration of isopropanol in the dilute solution, the vapor pressure of isopropanol, and Henry's law.
- A disadvantage in using isopropanol as the tracer compound is that it will not be known whether a significant leak occurred until after the cost of analyzing the sample has been spent. Elevated levels of isopropanol can also interfere with laboratory analytical method detection limits.

Option B - Helium

- The presence of helium within the sampling assembly should be monitored during purging and soil gas sample collection using a helium meter installed in-line with the sampling assembly. The meter should be positioned along the sampling line just before the personal sampling pump.
- Helium is readily available at a variety of retail businesses, is safe to use, and does not interfere with laboratory analytical method detection limits.
- A containment unit is constructed to cover the soil gas probe surface casing. The containment unit should consist of an overturned plastic pail set into a ring of dry bentonite to create a seal between the ground surface and the rim of the pail. The pail can be set directly on top of the sampling assembly tubing connected to the soil gas probe, which when pressed into the dry bentonite, should create a sufficient seal around the tubing. The pail will have two holes: one to allow for the introduction of helium; and the other to allow for air trapped inside the pail to escape while introducing the helium. The second hole will also allow insertion of the helium meter to measure the helium content within the pail.
- Prior to soil gas probe purging, helium will be introduced into the containment unit to obtain a minimum 50 percent helium content level. The helium content within the containment unit should be confirmed using the helium meter and recorded in the field logbook. Helium should continue to be introduced to the containment unit during soil gas probe purging and sampling and care should be taken not to increase the pressure within the containment unit beyond that of atmospheric pressure.
- During soil gas probe purging and sampling, the helium meter should be connected in-line with the sampling assembly. In the event that the helium meter measures a helium content with the sampling assembly of greater than 10 percent of the source concentration (i.e., 10 percent of the helium content measured within the containment unit), the soil gas probe will be judged to permit significant leakage such that the collected soil gas sample will not be considered reliable and representative of soil gas concentrations within the formation (ITRC, 2007).
- An advantage of using helium as the tracer compound is that a significant leak can be detected in the field and the cost of analyzing the Summa™ canister can be avoided.

Note: The 10 percent of the source concentration should be verified based on the applicable jurisdictional regulatory vapor intrusion guidance.

1.7.4 Sample Collection Procedure - Canister

1. Soil gas samples for assessing the vapor intrusion pathway must be collected using an acceptable canister, including certified clean Summa canisters. Only canisters certified clean at the 100 percent level can be used for soil gas sampling activities (i.e., pre-cleaned at the laboratory in accordance with U.S. EPA's TO-15 method and documentation of the cleaning activities will be provided by the laboratory). Summa canisters typically come in 1-, 1.7-, and 6-liter capacities, depending upon laboratory availability.

2. The canisters must be fitted with a laboratory-calibrated critical orifice flow regulation device sized to restrict the maximum soil gas sample collection flow rate to approximately 100 milliliters per minute (mL/min), which corresponds to the lower end of the maximum soil gas sampling flow rate recommended by Cal EPA (2015) of 100 to 200 mL/min. The 100 mL/min maximum flow rate is equivalent to sample collection times of 10, 17, or 60 minutes, respectively, for 1, 1.7, or 6 liter canister capacities. A maximum flow rate of 100 mL/min is recommended to limit VOC stripping from soil, prevent the short-circuiting of ambient air from ground surface down the soil gas probe annulus that would dilute the soil gas sample. A maximum flow rate of 100 mL/min increases confidence that the soil gas sample is drawn from immediately surrounding the screened interval.

3. A vacuum gauge should be supplied by the laboratory and used during sample collection to measure the initial canister vacuum, canister vacuum during sample collection, and residual canister vacuum at the end of sample collection. The vacuum gauge will be returned to the laboratory and used by the laboratory to measure the residual canister vacuum upon receipt of the canisters by the laboratory.

4. The canister should be connected to the soil gas probe valve at the surface casing using the sampling assembly (see Figure 15.18). The sampling assembly is connected using short lengths (e.g., 1-foot [0.3 m]) 1/4-inch (6.4 mm) or 3/8-inch (9.5 mm) diameter tubing (the tubing material will be Teflon® or nylon) and airtight stainless steel or brass tee-connectors and tee-valves (e.g., Swagelok® type). The canister should be connected to the soil gas probe along with a vacuum gauge and a personal sampling pump, all in series, using tee-connectors or tee-valves (in the order of soil gas probe, vacuum gauge, pump, and canister). A tee-valve should be used to connect the pump, which will allow the pump to be isolated from the sampling assembly during sample collection. Fresh tubing must be used for each sample.

5. Prior to collecting a soil gas sample, the stagnant air in the sampling assembly tubes and soil gas probe casing/sand pack must be removed. The soil gas probes should be purged prior to sampling using the personal sampling pump at a flow rate of less than 200 mL/min. A flow rate greater than 200 mL/min may be used when purging times are excessive, such as for deep wells with larger-diameter tubing. However, a vacuum of 100 inches of water (7.4 inches of Hg) or less must be maintained during sampling whenever a higher flow rate is used. This ensures that the collected soil gas sample is representative of actual soil gas concentrations within the formation. Measurements of the lengths and inner diameters of the above-ground sampling assembly and below-ground gas probe casing, screen, and sand pack should be used to calculate the "purge volume" (the purge volume will consider the pore volume of the sand pack assuming a 30 percent sand pack porosity). Prior to sample

collection, two to three purge volumes should be drawn from the probe/sample assembly, unless otherwise required by the applicable regulatory guidance. The purge data (calculated purge volume, purging rate, and duration of purging) should be recorded in the field logbook.

6. Prior to purging, a vacuum, or tightness, test should be conducted on the sampling assembly as the first of two leak-testing steps, as described further in Section 15.7.3. Briefly, this first leak-testing step (the vacuum test) should consist of opening the valve to the personal sampling pump leaving the valves to the Summa™ canister and the soil gas probe closed. The pump should then be operated to ensure that it draws no air from the sampling assembly (i.e., creates a negative pressure, or vacuum within the sampling assembly), thus establishing that all assembly connections are airtight. Further details of the vacuum test are described in Section 15.7.3.

7. Prior to purging, and following the vacuum test, the set-up for the second of the two leak-testing steps should be conducted. The second leak-testing step is the tracer compound step. A tracer compound is released at ground surface immediately around the soil gas probe surface casing. The tracer test is used to test for ambient air leakage down the annulus of the soil gas probe and into the soil gas sample. The tracer compound is either monitored using a meter connected in-line to the sampling assembly (e.g., helium), or is included as an analyte in the laboratory analysis of the soil gas samples (e.g., isopropanol). The setup requirements of the tracer compound leak-testing step are described in Section 15.7.3.

8. Following the vacuum test, and the setup for the tracer compound leak-testing step, the soil gas probe purging should commence by opening the valve to the soil gas probe and activating the personal sampling pump (and leaving closed the valve to the Summa™ canister). At the start and the end of the purging period, the total concentration of volatile organic vapors of the personnel sampling pump exhaust gas should be monitored using a portable photoionization detector (PID) meter. The PID meter should be connected in series after the personal sampling pump. Since typical PID instrument flow rates vary from approximately 300 to 500 mL/min (depending on the manufacturer and model), drawing a sample into the PID meter through the personal sampling pump will likely increase the purging flow rate temporarily, until a reading from the PID meter is obtained. PID readings should be recorded and entered in the field logbook and chain of custody form. The PID readings should provide the laboratory with an indication of whether a sample could require dilution before analysis.

9. Following purging, the valve to the personal sampling pump should be closed, and the valves to the soil gas probe and Summa™ canister opened to draw the soil gas sample into the canister. This should be completed concurrent with continued application of the leak-testing tracer compound. The vacuum gauge reading must be recorded during sample collection. Should the vacuum gauge reading remain elevated above 10 inches Hg for more than 30 minutes, this will be taken to indicate that the initial vacuum in the canister has not sufficiently dissipated, and that the soil screened by the soil gas probe does not produce sufficient soil gas to permit sample collection due to low permeability soil. If low permeability conditions are encountered, the probe can be sampled using the techniques outlined in Appendix D (Soil Gas Sampling in Low Permeability Soil) of Cal EPA (2015).

10. To ensure some residual vacuum in each canister following sample collection, the canister vacuum should be recorded at approximately 80 percent through the expected sample collection duration. With a 100 mL/min maximum flow rate, the expected sample collection duration would be 10, 17, or 60 minutes, respectively, for canister capacities of 1, 1.7, or 6 liters. A maximum residual vacuum of 10-inches Hg is allowed. A canister residual vacuum above this value will require continued sampling until vacuum reading is below this threshold, unless the vacuum remains above 10-inches Hg for more than 30 minutes, as described above. A minimum 0.5 to 1-inch Hg residual vacuum will be required for the sample to be considered valid, or the sampling will be repeated using a fresh Summa canister. Once the vacuum is measured, the safety cap must be securely tightened on the inlet of the Summa™ canister prior to shipment to the laboratory under chain-of-custody procedures.

Note: The 0.5 to 1-inch Hg residual vacuum should be verified based on the applicable jurisdictional regulatory vapor intrusion guidance.

11. The vacuum gauge provided by laboratory must be returned with the canister samples to check residual vacuum in the laboratory prior to sample analysis and recorded on the analytical data report. This check will ensure sample integrity prior to laboratory analysis, and that the canister has not become compromised during shipment to the laboratory.

12. If the critical orifice flow regulation devices (provided by the laboratory) and sampling assembly fittings/valves are to be re-used during sampling, they must be cleaned in accordance with laboratory requirements by purging with zero air (provided by laboratory) for minimum 45 seconds at minimum 75 psi (153 inches of Hg).

13. The canisters should be labeled noting the unique sample designation number, date, time, and sampler's initials. A bound field logbook should be maintained to record all soil gas sampling data.

14. The canisters should be listed on the chain-of-custody in order of suspected highest to lowest impact, as evidenced by the recorded PID readings. Indicate on the chain-of-custody for the laboratory to analyze the canisters in order from the lowest to highest PID reading.

The soil gas samples should be analyzed for the project-specified VOCs by the project laboratory using U.S. EPA's TO-15 gas chromatograph/mass spectrometer (GC/MS) methodology, with the mass spectrometer (MS) run in full scan mode. QA/QC measures implemented during the soil gas sampling event will include the two-step leak testing procedure (see Section 15.7.3), maintaining a minimum residual vacuum in the Summa™ canisters following sample collection, collection of one duplicate per sampling event or from at least 10 percent of the samples obtained, and collection of an ambient air sample (if needed). As an additional QA/QC measure, the laboratory should conduct a duplicate analysis of the sample collected in one of the canisters.

1.7.5 Sample Collection Procedure – Tedlar Bag

1. The low flow pump should be connected to the soil gas probe valve at the surface casing and the bag should be connected to the pump. The sampling assembly is connected using short lengths (e.g., 1-foot [0.3 m]) 1/4-inch (6.4 mm) or 3/8-inch (9.5 mm) diameter tubing (the

tubing material will be Teflon® or nylon) and airtight stainless steel or brass tee-connectors and tee-valves (e.g., Swagelok® type). Fresh tubing must be used for each sample.

2. Prior to collecting a soil gas sample, the stagnant air in the sampling assembly tubes and soil gas probe casing/sand pack must be removed. The soil gas probes should be purged prior to sampling using the personal sampling pump at a flow rate of less than 200 mL/min. A flow rate greater than 200 mL/min may be used when purging times are excessive, such as for deep wells with larger-diameter tubing. However, a vacuum of 100 inches of water (7.4 inches of Hg) or less must be maintained during sampling whenever a higher flow rate is used. This ensures that the collected soil gas sample is representative of actual soil gas concentrations within the formation. Measurements of the lengths and inner diameters of the above-ground sampling assembly and below-ground gas probe casing, screen, and sand pack should be used to calculate the "purge volume" (the purge volume will consider the pore volume of the sand pack assuming a 30 percent sand pack porosity). Prior to sample collection, two to three purge volumes should be drawn from the probe/sample assembly, unless otherwise required by the applicable regulatory guidance. The purge data (calculated purge volume, purging rate, and duration of purging) should be recorded in the field logbook.

3. Prior to purging, a vacuum, or tightness, test should be conducted on the sampling assembly as the first of two leak-testing steps, as described further in Section 15.7.3. Briefly, this first leak-testing step (the vacuum test) should consist of opening the valve to the personal sampling pump leaving the valves to the bag and the soil gas probe closed. The pump should then be operated to ensure that it draws no air from the sampling assembly (i.e., creates a negative pressure, or vacuum within the sampling assembly), thus establishing that all assembly connections are airtight. Further details of the vacuum test are described in Section 15.7.3.

4. Prior to purging, and following the vacuum test, the set-up for the second of the two leak-testing steps should be conducted. The second leak-testing step is the tracer compound step. A tracer compound is released at ground surface immediately around the soil gas probe surface casing. The tracer test is used to test for ambient air leakage down the annulus of the soil gas probe and into the soil gas sample. The tracer compound is either monitored using a meter connected in-line to the sampling assembly (e.g., helium), or is included as an analyte in the laboratory analysis of the soil gas samples (e.g., isopropanol). The setup requirements of the tracer compound leak-testing step are described in Section 15.7.3.

5. Following the vacuum test, and the setup for the tracer compound leak-testing step, the soil gas probe purging should commence by opening the valve to the soil gas probe and activating the personal sampling pump (and disconnecting the bag). At the start and the end of the purging period, the total concentration of volatile organic vapors of the personnel sampling pump exhaust gas should be monitored using a portable photoionization detector (PID) meter. The PID meter should be connected in series after the personal sampling pump. Since typical PID instrument flow rates vary from approximately 300 to 500 mL/min (depending on the manufacturer and model), drawing a sample into the PID meter through the personal sampling pump will likely increase the purging flow rate temporarily, until a reading from the PID meter is obtained. PID readings should be recorded and entered in the

field logbook and chain of custody form. The PID readings should provide the laboratory with an indication of whether a sample could require dilution before analysis.

6. Following purging, the bag should be reconnected to the personal sampling pump and the valves to the soil gas probe opened to draw the soil gas sample into the bag. This should be completed concurrent with continued application of the leak-testing tracer compound. Should the bag not inflate for more than 30 minutes, this will be taken to indicate that the soil screened by the soil gas probe does not produce sufficient soil gas to permit sample collection due to low permeability soil. If low permeability conditions are encountered, the probe can be sampled using the techniques outlined in Appendix D (Soil Gas Sampling in Low Permeability Soil) of Cal EPA (2015).
7. If the pump and sampling assembly fittings/valves are to be re-used during sampling, they must be cleaned in accordance with laboratory requirements by purging with zero air (provided by laboratory) for minimum 45 seconds at minimum 75 psi (153 inches of Hg).
8. The bags should be labeled noting the unique sample designation number, date, time, and sampler's initials. A bound field logbook should be maintained to record all soil gas sampling data.
9. The bags should be listed on the chain-of-custody in order of suspected highest to lowest impact, as evidenced by the recorded PID readings. Indicate on the chain-of-custody for the laboratory to analyze the canisters in order from the lowest to highest PID reading.

The soil gas samples should be analyzed for the project-specified VOCs by the project laboratory using U.S. EPA's TO-15 gas chromatograph/mass spectrometer (GC/MS) methodology, with the mass spectrometer (MS) run in full scan mode. QA/QC measures implemented during the soil gas sampling event will include the two-step leak testing procedure (see Section 15.7.3), collection of one duplicate per sampling event or from at least 10 percent of the samples obtained, and collection of an ambient air sample (if needed). As an additional QA/QC measure, the laboratory should conduct a duplicate analysis of the sample collected in one of the bags.

1.7.6 Sample Collection Procedure – Syringe

1. The syringe should be connected to the soil gas probe valve at the surface casing. The sampling assembly is connected using short lengths (e.g., 1-foot [0.3 m]) 1/4-inch (6.4-mm) or 3/8-inch (9.5-mm) diameter tubing (the tubing material will be Teflon® or nylon) and airtight stainless steel or brass tee-connectors and tee-valves (e.g., Swagelok® type). Fresh tubing must be used for each sample.
2. Prior to collecting a soil gas sample, the stagnant air in the sampling assembly tubes and soil gas probe casing/sand pack must be removed. The soil gas probes should be purged prior to sampling using the personal sampling pump at a flow rate of less than 200 mL/min. A flow rate greater than 200 mL/min may be used when purging times are excessive, such as for deep wells with larger-diameter tubing. However, a vacuum of 100 inches of water (7.4 inches of Hg) or less must be maintained during sampling whenever a higher flow rate is used. This ensures that the collected soil gas sample is representative of actual soil gas concentrations within the formation. Measurements of the lengths and inner diameters of the above-ground sampling assembly and below-ground gas probe casing, screen, and sand

pack should be used to calculate the "purge volume" (the purge volume will consider the pore volume of the sand pack assuming a 30 percent sand pack porosity). Prior to sample collection, two to three purge volumes should be drawn from the probe/sample assembly, unless otherwise required by the applicable regulatory guidance. The purge data (calculated purge volume, purging rate, and duration of purging) should be recorded in the field logbook.

3. Prior to purging, a vacuum, or tightness, test should be conducted on the sampling assembly as the first of two leak-testing steps, as described further in Section 15.7.3. Briefly, this first leak-testing step (the vacuum test) should consist of opening the valve to the personal sampling pump leaving the valves to the syringe and the soil gas probe closed. The pump should then be operated to ensure that it draws no air from the sampling assembly (i.e., creates a negative pressure, or vacuum within the sampling assembly), thus establishing that all assembly connections are airtight. Further details of the vacuum test are described in Section 15.7.3.

4. Prior to purging, and following the vacuum test, the set-up for the second of the two leak-testing steps should be conducted. The second leak-testing step is the tracer compound step. A tracer compound is released at ground surface immediately around the soil gas probe surface casing. The tracer test is used to test for ambient air leakage down the annulus of the soil gas probe and into the soil gas sample. The tracer compound is either monitored using a meter connected in-line to the sampling assembly (e.g., helium), or is included as an analyte in the laboratory analysis of the soil gas samples (e.g., isopropanol). The setup requirements of the tracer compound leak-testing step are described in Section 15.7.3.

5. Following the vacuum test, and the setup for the tracer compound leak-testing step, the soil gas probe purging should commence by opening the valve to the soil gas probe and activating the personal sampling pump (and disconnecting the bag). At the start and the end of the purging period, the total concentration of volatile organic vapors of the personnel sampling pump exhaust gas should be monitored using a portable photoionization detector (PID) meter. The PID meter should be connected in series after the personal sampling pump. Since typical PID instrument flow rates vary from approximately 300 to 500 mL/min (depending on the manufacturer and model), drawing a sample into the PID meter through the personal sampling pump will likely increase the purging flow rate temporarily, until a reading from the PID meter is obtained. PID readings should be recorded and entered in the field logbook and chain of custody form. The PID readings should provide the laboratory with an indication of whether a sample could require dilution before analysis.

6. Following purging, the valve to the syringe should be opened and soil gas should be draw into the syringe at a rate of approximately 60 mL/min. This should be completed concurrent with continued application of the leak-testing tracer compound.

7. If the sampling assembly fittings/valves are to be re-used during sampling, they must be cleaned in accordance with laboratory requirements by purging with zero air (provided by laboratory) for minimum 45 seconds at minimum 75 psi (153 inches of Hg).

8. The syringes should be labeled noting the unique sample designation number, date, time, and sampler's initials. A bound field logbook should be maintained to record all soil gas sampling data.

9. The syringes should be listed on the chain-of-custody in order of suspected highest to lowest impact, as evidenced by the recorded PID readings. Indicate on the chain-of-custody for the laboratory to analyze the canisters in order from the lowest to highest PID reading.

The soil gas samples should be analyzed for the project-specified VOCs by the project laboratory using U.S. EPA's TO-15 gas chromatograph/mass spectrometer (GC/MS) methodology, with the mass spectrometer (MS) run in full scan mode. QA/QC measures implemented during the soil gas sampling event will include the two-step leak testing procedure (see Section 15.7.3), collection of one duplicate per sampling event or from at least 10 percent of the samples obtained, and collection of an ambient air sample (if needed). As an additional QA/QC measure, the laboratory should conduct a duplicate analysis of the sample collected in one of the syringes.

1.7.7 Follow-Up Activities

The following activities should be performed at the completion of the field work.

1. Review and compare newly obtained data with historic data and flag unusual or extreme readings for review.
2. Soil gas concentrations are reported in units of µg/m^3 or ppbv. Unlike concentration units for groundwater, these units are not directly interchangeable. The molecular weight of the compound in question is a factor in the conversion from units of mass per unit volume to parts per billion by volume.
3. Ensure site access keys are returned.
4. The equipment should be cleaned and returned to the Equipment Coordinator. All equipment should be cleaned at the site.
5. Monitoring forms and field notes should be sent to the file. The field book should be stored at the appropriate GHD office.

1.8 References

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Appendix D
Quality Assurance Project Plan

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QAPP Distribution List

Name/Organization	**Number of Copies**
_____ - GHD Project Manager	1
_____ - GHD Field Quality Assurance Officer	1
_____ - GHD Quality Assurance Officer	1
_____ - Laboratory Project Manager	1
_____ - Regulatory Agency	1

Quality Assurance Project Plan
Soil Vapor Investigation
Phillips 66/Former Tidewater Site
Seattle, Washington
Revision Number 0
August 2018

Prepared By: GHD Services Inc. (GHD)

Approved By: _____ Date: _____

GHD Project Manager

Approved By: _____ Date: _____

GHD Quality Assurance/Quality Control Officer

Approved By: _____ Date: _____

GHD Field Quality Assurance Officer

Approved By: _____ Date: _____

Laboratory Project Manager

Approved By: _____ Date: _____

Laboratory Quality Assurance Officer

1. Introduction

This Quality Assurance Project Plan (QAPP) presents the policies, organization, objectives, functional activities, and Quality Assurance/Quality Control (QA/QC) activities designed to achieve the specific data quality goals associated with the Soil Vapor Investigation. The Soil Vapor Investigation addresses soil, groundwater, and soil vapor data collection at the former Tidewater Service Station located at 2800 Martin Luther King Jr. Way, Seattle, King County, Washington previously known as the Phillips 66 070644 Site.

The objectives of this QAPP are to provide sufficiently thorough and concise descriptions of the measures to be applied during soil, groundwater, and soil vapor investigation such that the data generated will be of a known and acceptable level of precision and accuracy. This QAPP provides comprehensive information regarding the project personnel responsibilities, and sets forth specific procedures to be used during sampling of relevant environmental matrices and analyses of data.

The remaining sections of the QAPP outline the analytical activities and responsibilities for this investigation and are organized as follows:

Section 2 - Objectives of Investigation: references the Soil Vapor Investigation Work Plan regarding the objectives of the investigation.

Section 3 - Project Organization: describes the key project personnel and their duties.

Section 4 - Data Quality Objectives: summarizes the quality assurance objectives to achieve the required accuracy and precision.

Section 5 - Sampling Design: references the sampling design described in the Soil Vapor Investigation Work Plan.

Section 6 - Special Training/Certification: describes the field and laboratory training requirements.

Section 7 - Field Procedures: describes the documentation required for samples during collection, transport, and storage at the laboratory. Actual field procedures are described in the Field Sampling Plan (FSP).

Section 8 - Laboratory Procedures: provides a description of the analytical methodologies to be used for the investigation. Summarizes instrument calibration and analyte identification and quantitation.

Section 9 - Quality Control: describes the different types of field and laboratory quality control required for the project.

Section 10 - Data Management Procedures: provides a summary of the laboratory's data flow from bench to final report, document control, and quality control check points.

Section 11 - Audits: describes the internal laboratory audits.

Section 12 - Data Review, Verifications, and Validation: provides a general overview of the validation of the laboratory data.

Section 13 - Data Quality Assessment: provides a summary of QA/QC topics to be included in the final report. Contains formulas for precision, accuracy, and completeness.

Section 14 - Preventive Maintenance: provides a brief description of maintenance on laboratory and field instrumentation and its documentation.

Section 15 - Corrective Action: provides a summary of the steps necessary for corrective actions.

2. Objectives of Investigation

Sections 2 and 3 of the Soil Vapor Investigation Work Plan describe the objectives of the investigation.

3. Project Organization

A brief description of the duties of the key project personnel is presented below.

GHD Project Manager

- Provides day-to-day project management
- Provides managerial guidance to the GHD QA/QC Officer
- Prepares and reviews reports
- Conducts preliminary chemical data interpretation and assessment
- Responsible for overall project completion in accordance with the approved design

GHD Quality Assurance/Quality Control Officer

- Oversees and reviews laboratory activities
- Determines laboratory data corrective action
- Performs analytical data validation and assessment
- Reviews laboratory QA/QC
- Assists in preparation and review of final report
- Provides technical representation for analytical activities
- Provides managerial and technical guidance to the Field Sampling Supervisor
- Maintains officially approved QAPP document

Field Sampling Supervisor

- Provides immediate supervision of all on-Site activities
- Provides field management of sample collection and field QA/QC
- Provides technical representation for field activities

- Is responsible for maintenance of the field equipment
- Responsible that all field personnel are properly trained and certified

Laboratory - Project Manager, Analytical Contractor

- Ensures resources of laboratory are available on an as-required basis
- Coordinates laboratory analyses
- Supervises laboratory's in-house chain of custody
- Schedules analyses of samples
- Oversees review of data
- Oversees preparation of analytical reports
- Approves final analytical reports

Laboratory - Quality Assurance/Quality Control Officer, Analytical Contractor

- Overviews laboratory QA/QC
- Overviews QA/QC documentation
- Conducts detailed data review
- Decides laboratory corrective actions, if required
- Provides technical representation for laboratory QA/QC procedures
- Keeps up-to-date training records of analysts

Laboratory - Sample Custodian - Analytical Contractor

- Receives and inspects the sample containers
- Records the condition of the sample containers
- Signs appropriate documents
- Verifies chain of custody and their correctness
- Notifies Laboratory Project Manager and Laboratory QA/QC Officer of sample receipt and inspection
- Assigns a unique laboratory identification number correlated to the field sample identification number and enters each into the sample receiving log
- Initiates transfer of samples to the appropriate lab sections with assistance from the Laboratory Project Manager
- Controls and monitors access to and storage of samples and extracts

The analytical laboratories selected to perform the analyses will be Pace Analytical Services (Pace) and ALS Environmental Laboratory (ALS). Soil vapor analyses will be performed by ALS at the Simi Valley, California location. The soil and the groundwater analyses will be performed by Pace at

the Minneapolis, Minnesota location. ALS and Pace are accredited under the State of Washington Department of Ecology (WDOE) Environmental Laboratory Accreditation Program.

4. Data Quality Objectives (DQO)

4.1 Quality Assurance Objectives for Measurement Data

The overall quality assurance objective is to develop and implement procedures for sample collection and analyses, which will provide data with an acceptable level of accuracy and precision.

Quality assurance measures for this project will begin with sample containers. Soil and groundwater sample containers will be purchased from a certified manufacturer and will be pre-cleaned (I-Chem Series 200 or equivalent). Soil vapor canisters will be rented from the laboratory. Rented canisters will be certified batched cleaned according to United States Environmental Protection Agency (USEPA) Method TO-15.

4.2 Laboratory Quality Assurance

The following subsections define the quality assurance goals required to meet the DQOs of the project. A copy of the laboratory's Standard Operating Procedure (SOP) is presented in Attachment A.

4.2.1 Accuracy, Precision, and Sensitivity of Analyses

The fundamental quality assurance objective with respect to the accuracy, precision, and sensitivity of analytical data is to meet the quality control acceptance criteria of each analytical protocol. Summaries of the targeted quantitation limits are provided in Tables 4.1 (groundwater), 4.2 (soil), and 4.3 (vapor). It should be noted that these limits are targeted quantitation limits only; limits are highly matrix dependent and may not always be achieved.

The method accuracy (percent recovery) will be determined by spiking blank canisters and selected soil and groundwater samples (matrix spikes) with the compounds of interest. Accuracy will be reported as the percent recovery of the spiking compounds and will compare with the criteria given in the appropriate methods, as identified in Section 8. The mathematical formula for accuracy is presented in Section 13.1.2.

The methods precision (reproducibility between duplicate analyses) will be determined based on the duplicate analysis of matrix spike samples of soil and groundwater and a duplicate analysis of a soil vapor sample. Precision will be reported as Relative Percent Differences (RPDs) between duplicate results. The mathematical formula for precision is presented in Section 13.1.1.

4.2.2 Completeness, Representativeness, and Comparability

A completeness requirement of 90 percent will be targeted for the program (see Section 13.1.3 for definition and mathematical formula of completeness).

The quantity of samples to be collected has been estimated in an effort to effectively represent the population being studied. Summaries of the sampling and analysis programs are presented in Table 4.3.

Analytical methods selected for this study are consistent with those used for previous studies (if applicable) to assure comparability of the data. All standards used by the laboratory will be traceable to reliable sources and will be checked with an independent standard.

4.3 Field Measurement Quality Assurance

Measurement data will be generated during field activities. These activities include, but are not limited to, the following:

i) Temperature

ii) pH

iii) Conductivity

iv) Turbidity

v) Oxidation-reduction potential

vi) Dissolved oxygen

vii) Salinity

viii) Documenting time and weather conditions

ix) Observation of sample location appearance and other conditions

The general quality assurance objective for measurement data is to obtain reproducible and comparable measurements to a degree of accuracy consistent with the use of standardized procedures.

5. Sampling (Experimental) Design

The sampling design is described in Section 3 of the Soil Vapor Investigation Work Plan.

6. Special Training/Certification

GHD field personnel all hold current hazardous waste site operation (HAZWOPER) certification required by 29CFR 1910.120. GHD field personnel also undergo an extensive training program. Field personnel must first read the SOPs and attend a series of live seminars and CD-ROM courses on fieldwork topics that need to be monitored. A practical demonstration of skills learned must be provided in the field to senior staff three times, in order for field personnel to be able to work independently. These training requirements pertain to sampling procedures and the calibration/operation of field instrumentation. Field training records are stored electronically per the GHD Quality System.

7. Field Procedures

The field procedures are presented in the FSP.

The sample container, shipping, and packaging requirements are identified in Table 7.1 and in Section 7.1.3.

The following subsections define sample custody and document control.

7.1 Sample Custody and Document Control

The following documentation procedures will be used during sampling and analysis to provide chain of custody control during transfer of samples from collection through storage. Recordkeeping documentation will include use of the following:

i) Field logbooks (bound with numbered pages) to document sampling activities in the field

ii) Labels to identify individual samples

iii) Chain of custody record sheet to document analyses to be performed

iv) Laboratory sample custody logbook

7.1.1 Field Logbook

In the field, the sampler will record the following information in the field logbook (bound) for each sample collected:

i) Project number

ii) Sample matrix

iii) Name of sampler

iv) Sample source

v) Time and date

vi) Pertinent data (i.e., sampling duration)

vii) Analysis to be conducted

viii) Sampling method

ix) Appearance of each sample (e.g., color, particulates, effervescing)

x) Preservation added, if any

xi) Number of sample bottles collected

xii) Pertinent weather data

Each field logbook page will be signed by the sampler. Each logbook is stored in a filing cabinet located in GHD's Tacoma office per the GHD Quality System.

7.1.2 Sample Numbering

A unique sample numbering system will be used to identify each collected sample. This system will provide a tracking number to allow retrieval and cross-referencing of sample information. The sample numbering system to be used is described as follows:

Example: WG-011618-AA-BBB-XXX

Where: WG - Designates sample type
(WG=Groundwater, SG=Soil Gas, TB=Trip Blank, FD=Field Duplicate)

011618: Date of collection (mm/dd/yy)

AA: Sampler initials

BBB: Location I.D.

XXX: Unique sample number

All field samples will be numbered with a unique sample number.

Field duplicates will be submitted blind to the laboratory. The field duplicate location will be specified in the field notebook and on the field sample key submitted to data management.

7.1.3 Chain of Custody Records

Chain of custody forms will be completed for all samples collected during the program.

The chain of custody form will document the transfer of sample containers. Custody seals will be placed on each cooler (or box). The cooler (or box) will then be sealed with packing tape. Sample container labels will include sample number, place of collection, and date and time of collection. All samples should be delivered to the laboratory by same day or overnight delivery.

The chain of custody record, completed at the time of sampling, will contain, but not be limited to, the sample number, date and time of sampling, and the name of the sampler. The chain of custody document will be signed, timed, and dated by the sampler when transferring the samples.

Each sample cooler (or box) being shipped to the laboratory will contain a chain of custody form. The chain of custody form will consist of four copies which will be distributed as follows: The shipper will maintain a copy while the other three copies will be enclosed in a waterproof envelope within the cooler (or box) with the samples. The shipper's copy will be filed in the field project folder located in GHD's Tacoma office per the GHD Quality System. The cooler (or box) will then be sealed properly for shipment. The laboratory, upon receiving the samples, will complete the three remaining copies. The laboratory will retain one copy for their records. The laboratory will return one copy to the GHD QA/QC Officer upon receipt of the samples. One copy will be returned with the data deliverables package.

Upon receipt of the cooler (or box) at the laboratory, the Sample Custodian will inspect the shipping cooler (or box) and the custody seal. The Sample Custodian will note the condition of the cooler (or box) and the custody seal on the chain of custody record sheet. If the shipping cooler (or box)

seal is intact, the sample containers will be accepted for analyses. The Sample Custodian will document the date and time of receipt of the container and sign the form.

If damage or discrepancies are noticed (including sample temperature exceedances), they will be recorded in the remarks column of the record sheet, dated, and signed. Any damage or discrepancies will be reported to the Laboratory Project Manager and Laboratory QA/QC Officer before samples are processed.

7.1.4 Sample Documentation in the Laboratory

Each sample or group of samples shipped to the laboratory for analysis will be given a unique identification number. The Sample Custodian will record the client name, number of samples, and date of receipt of samples in the Sample Control Logbook. Samples removed from storage for analyses will be documented in the Sample Control Logbook.

The laboratory will be responsible for maintaining analytical logbooks and laboratory data as well as a sample (on hand) inventory for submittal to the GHD QA/QC Officer on an "as-required" basis. Raw laboratory data produced from the analysis of samples submitted for this program will be inventoried and maintained by the laboratory for a period of 5 years at which time the GHD QA/QC Officer will advise the laboratory regarding the need for additional storage.

7.1.5 Storage of Samples

After the Sample Custodian has completed the chain of custody forms and the incoming sample log, the chain of custody will be checked to ensure that all samples are stored in the appropriate locations. All samples will be stored within an access controlled custody room.

7.1.6 Sample Documentation

Evidentiary files for the entire project shall be inventoried and maintained by the GHD QA/QC Officer and shall consist of the following:

i) Project related plans

ii) Project logbooks

iii) Field data records

iv) Sample identification documents

v) Chain of custody records

vi) Report notes, calculations, etc.

vii) Lab data, etc.

viii) References, copies of pertinent literature

ix) Miscellaneous - photos, maps, drawings, etc.

x) A copy of all final reports pertaining to the project

7.1.7 Field Instrumentation

Field equipment used during this investigation will be calibrated both prior to and following the day's surveys in accordance with the manufacturer's instructions. The equipment will also be operated in accordance with the manufacturer's instructions. Records of calibrations of field equipment will be recorded in a bound field notebook.

8. Laboratory Procedures

8.1 Analytical Methods

Investigative samples will be analyzed for the parameters listed in Tables 4.1, 4.2, and 4.3 using the methods cited in Table 4.4. These methods have been selected to meet the DQOs for each sampling activity.

Data deliverables for this program will include final results for the investigative samples and corresponding quality control parameters as specified in Section 10.2.

8.2 Calibration Procedures and Frequency

8.2.1 Instrument Calibration

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. Each instrument is calibrated with standard solutions appropriate to the type of instrument and the linear range established for the analytical method. The frequency of calibration and the concentration of calibration standards are determined by the manufacturer guidelines, the analytical method, or the requirements of special contracts.

A bound notebook will be kept with each instrument requiring calibration in which will be recorded activities associated with quality assurance monitoring and repairs program. These records will be checked during periodic equipment review and internal and external QA/QC audits.

8.2.2 Gas Chromatography/Mass Spectrometry (GC/MS)

It is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria prior to initiating any ongoing data collection. This is accomplished through the analyses of tuning compounds as specified in the analytical methods.

Calibration of the GC/MS system will consist of an initial calibration curve utilizing at least 5 points. The initial calibration curve for each compound of interest will be verified at the beginning of the day or with each 12 hours (24 hours for method TO-15) of instrument operating time.

All method-specified calibration criteria must be met prior to sample analyses. All calibrations must be performed using either average response factors or first-order linear regression (with a correlation coefficient requirement of 0.99). Higher order fits will not be allowed unless the laboratory can demonstrate that the instrument is working properly and that the instrument response over the concentration range of interest is second-order.

Quantification of samples that are analyzed by GC/MS will be performed by internal standard calibration. For quantitation, the nearest internal standard free of interferences must be used.

8.2.3 Gas Chromatography

Quantification for samples that are analyzed by GC with element selective detectors shall be performed by external standard calibration. Standards containing the compounds of interest will be analyzed at a minimum of five concentrations to establish the linear range of the detector. Single point calibration will be performed at the beginning of each day and at every tenth injection. The response factors from the single point calibration will be checked against the average response factors from multi-level calibration. If deviations in response factors are outside the limits allowed by the analytical method protocols, then system recalibration will be performed. Alternatively, fresh calibration standards will be prepared and analyzed to verify instrument calibration.

All method-specified calibration criteria must be met prior to sample analyses. All calibrations must be performed using either average response factors or first-order linear regression (with a correlation coefficient requirement of 0.995). Higher order fits will not be allowed unless the laboratory can demonstrate that the instrument is working properly, and that the instrument response over the concentration range of interest is second-order.

8.3 Compound Identification

Compounds, which will be analyzed by GC/MS, will be identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard references should be obtained on the user's GC/MS within the same 12 hours (24 hours for method TO-15) as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. The following criteria must be satisfied to verify identification:

i) The relative retention time (RRT) of the sample component is within ±0.06 RRT units of the RRT of the standard component.

ii) Correspondence of the sample component and the standard component mass spectrum.

For GC determinations of specific analytes, the RRT of the unknown will be compared with that of an authentic standard. Since a true identification by GC is not possible, an analytical run for compound confirmation will be followed according to the specifications in the methods. Peaks must elute within daily retention time windows established for each indicator parameter to be declared a tentative or confirmed identification. Retention time windows are determined using standard protocols defined in each method.

8.4 Quantitation

The procedures for quantitation of analytes are discussed in the appropriate analytical methods. Sample results are calculated using either an external standard or an internal standard technique. External standard techniques directly compare the response from the sample to the response of the target analyte in the calibration standards. Internal standard technique utilizes the addition of a compound that resembles the target compound but is not commonly found in nature. This

compound is added to all standards, samples, and quality control samples. Quantitation is based on the ratio of the target compound in the sample to the response of the internal standard in the sample compared to a similar ratio derived for each calibration standard.

8.5 Quantitation Limit Requirements

Targeted method reporting limits (MRLs) will be consistent with those presented in Tables 4.1, 4.2, and 4.3. When matrix interferences are noted during sample analysis, actions will be taken by the laboratory to achieve the specified quantitation limits. Samples will not be diluted by more than a factor of five to reduce matrix effects.

Samples may be diluted to a greater extent if the concentrations of analytes of concern exceed the calibration range of the instrument. In such cases, the Laboratory QA/QC Officer will assure that the laboratory demonstrates good analytical practices and such practices are documented in order to achieve the specified quantitation limits.

9. Quality Control

9.1 Quality Control for Laboratory Analyses

Specific procedures related to internal laboratory quality control samples are described in the following subsections. The types and frequency of quality control samples is presented in Table 4.4. The laboratory is not limited to what is specified on the table, but must include it.

9.1.1 Method Blanks

A method blank will be analyzed by the laboratory at a frequency of one blank per each group of up to 20 samples analyzed or prepared at the same time. The method blank will be carried through the entire analytical procedure. No compound of interest should be detected above the quantitation limit. If a positive result is calculated, the laboratory will contact the GHD QA/QC Officer for further instructions.

9.1.2 Laboratory Control Sample/Duplicate Analyses

A laboratory control sample will be analyzed for all compounds of interest. A laboratory duplicate will be analyzed at a minimum frequency of one per analytical batch. Where method specified limits were not available, general control limits will be used. Percent recoveries will be used to evaluate analytical accuracy while the RPD between duplicate analyses will be used to assess analytical precision.

9.1.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Analyses

An MS/MSD sample will be analyzed for all parameters, where applicable. MS/MSD or laboratory duplicate will be analyzed at a minimum frequency of one per analytical batch. Acceptable criteria and analytes that will be used for matrix spikes are identified in the methods (see Table 4.4 for methods). Where method specified limits were not available, general control limits will be used.

Percent spike recoveries will be used to evaluate analytical accuracy, while the RPD between duplicate analyses will be used to assess analytical precision.

9.1.4 Surrogate Analyses

Surrogates are organic compounds which are similar to the analytes of interest, but which are not normally found in environmental samples. Surrogates are added to samples to monitor the effect of the matrix on the accuracy of the analysis. Every blank, standard, and environmental sample analyzed by GC or GC/MS, including MS/MSD samples, will be spiked with surrogate compounds prior to sample preparation.

The compounds that will be used as surrogates and the levels of recommended spiking are specified in the methods. Surrogate spike recoveries must fall within the control limits specified in the methods (see Table 4.4 for methods). If any recoveries are excessively low (<10 percent), or if all recoveries in a sample are low, the laboratory will reanalyze the sample.

9.2 Quality Control for Field Sampling

To assess the quality of data resulting from the field sampling program, field duplicate and trip blanks samples will be collected and submitted to the analytical laboratory as blind samples.

9.2.1 Field Duplicate Samples

Field duplicate samples will be collected and used to assess the aggregate precision of sampling techniques and laboratory analysis. For every 20 investigative samples, a field duplicate sample will be collected and submitted blind to the laboratory. Field duplicates will be assessed using an RPD of ±30 percent for groundwater, ±50 percent for soil, and ±20 for soil vapor.

9.2.2 Trip Blank Sample Analysis

Trip blank samples will be collected with the groundwater samples to evaluate contamination from sample collection, transportation, storage, and analytical activities. One trip blank will be submitted per sample cooler.

9.3 Quality Control Documentation

All quality control results will be reported as part of the data package. All results will be tabulated and reported using Contract Laboratory Program (CLP)-like forms where applicable. Section 10.2 describes the requirements of the data package.

9.4 Inspection/Acceptance of Supplies and Consumables

Critical supplies and consumables for this project include field equipment, such as meters and pumps, decontamination reagents, sample bottles, and laboratory standards. The laboratory follows strict SOPs that define log in, preparation, and tracking of standards. Field equipment that is supplied by pre-approved vendors is maintained and calibrated by the vendor. All GHD-owned field equipment and reagents used in the field are ordered through the equipment manager per the GHD Quality System. The equipment manager is responsible for maintaining and calibrating all

GHD-owned field instruments. All maintenance and calibrations are documented and filed. All field reagents are maintained by the equipment manager and tracked per the GHD Quality System. All field instrumentation is calibrated again in the field prior to use. This calibration is documented in the logbook and on the proper Quality System form, which is kept in the main project file.

10. Data Management Procedures

10.1 General

The contract laboratory will perform internal data verification and data review under the direction of the Laboratory QA/QC Officer. The Laboratory QA/QC Officer will be responsible for assessing data quality and advising of any data which were rated "preliminary" or "unacceptable" or other qualifications based on the quality control criteria outlined in the relevant methods, which would caution the data user of possible unreliability. Data reduction, verification, and reporting by the laboratory will be conducted as detailed in the following:

i) Raw data produced and checked by the responsible analysts is turned over for independent review by another analyst.

ii) The area supervisor reviews the data for attainment of quality control criteria presented in the referenced analytical methods.

iii) Upon completion of all reviews and acceptance of the raw data by the laboratory operations manager, a computerized report will be generated and sent to the Laboratory QA/QC Officer.

iv) The Laboratory QA/QC Officer will complete a thorough inspection of all reports.

v) The Laboratory QA/QC Officer and area supervisor will decide whether any sample reanalysis is required.

vi) Upon acceptance of the preliminary reports by the Laboratory QA/QC Officer, final reports will be generated and signed by the Laboratory Project Manager.

10.2 Laboratory Reporting, Data, Presentation, and Final Report

Reporting and deliverables shall include, but not be limited to, all items listed in Table 10.1.

All sample data and corresponding QA/QC data as specified in the analytical methods, shall be maintained accessible either in hard copy and/or computer data files.

The laboratory will submit an electronic submission of the data within 15 business days of receipt of the final sample included in the sample delivery group (SDG). An SDG will consist of 20 field samples or all samples collected over a period of a week, whichever occurs first. All due dates will be calculated from the Friday of every sampling event. An electronic copy of the results and quality control will be in EQuIS format.

10.3 Document Control System

A document control system ensures that all documents are accounted for when the project is complete.

A project number will be assigned to the project. This number will appear on sample identification tags, logbooks, data sheets, control charts, project memos, analytical reports, document control logs, corrective action forms and logs, quality assurance plans, and other project analytical records. With the exception of field related documents, all documents are electronically stored per the GHD Quality System. Field related documents are stored at GHD's Tacoma office.

Electronic deliverables are maintained on a secured drive of the GHD network and are only accessible to approved GHD personnel. Electronic data deliverables are uploaded into a main project database. The database is only accessible to approved database personnel.

10.4 Quality Control Check Points and Data Flow

The following specific quality control checkpoints will be common to all analyses. They are presented with the decision points.

Chemist - Bench Level Checks

- Systems Check: sensitivity, linearity, and reproducibility within specified limits
- Duplicate analyses within control limits
- Blank spike results within control limits
- Calculation/data reduction checks: calculations cross-checked, any discrepancies between forms and results evident, results tabulated sequentially on the correct forms

Laboratory Project Manager

- Systems operating within limits
- Data transcription correct
- Data complete
- Data acceptable

Sample Control

- Samples returned to sample control following analysis

Laboratory Quality Assurance/Quality Control Officer

- Quality assurance objectives met
- Quality control checks are completed
- Final data and report package is complete

11. Audits

For the purpose of external evaluation, performance evaluation check samples are analyzed periodically by the laboratory. Internally, the evaluation of data from these samples is done on a continuing basis over the duration of a given project.

The GHD QA/QC Officer may carry out performance and/or systems audits to insure that data of known and defensible quality are consistently produced during this program.

Systems audits are qualitative evaluations of all components of field and laboratory quality control measurement systems. They determine if the measurement systems are being used appropriately. The audits may be carried out before all systems are operational during the program or after completion of the program. Such audits typically involve a comparison of the activities given in the QA/QC Plan described herein, with activities actually scheduled or performed. A special type of systems audit is the data management audit. This audit addresses only data collection and management activities.

The performance audit is a quantitative evaluation of the measurement systems used for a monitoring program. It requires testing the measurement systems with samples of known composition or behavior to quantitatively evaluate precision and accuracy. A performance audit may be carried out by or under the auspices of the GHD QA/QC Officer without the knowledge of the analyst during each sampling event for this program.

It should be noted, however, that any additional external quality assurance audits will only be performed if deemed necessary.

12. Data Review, Verification, and Validation

12.1 General

Validation of the analytical data will be performed by the GHD QA/QC Officer. The data validation will be performed in accordance with the methods and guidance from the document, "USEPA National Functional Guidelines for Superfund Organic Methods Data Review", EPA 540-R-2016-002, September 2016.

Data associated with the investigation will receive a Level IV validation that includes checking all raw data and recalculations of results. Assessment of analytical and in-house data will include checks on data consistency by looking for comparability of duplicate analyses, comparability to previous data from the same sampling location (if available), adherence to accuracy and precision control criteria detailed in this QAPP and anomalously high or low parameter values. The results of these data validations will be reported to the Project Manager and the contract laboratory, noting any discrepancies and their effect upon acceptability of the data.

Raw data from field measurements and sample collection activities that are used in project reports will be appropriately identified and appended to the report. Where data have been reduced or

summarized, the method of reduction will be documented in the report. Field data will be audited for anomalously high or low values that may appear to be inconsistent with other data.

13. Data Quality Assessment

Final reports will contain a discussion on QA/QC summarizing the quality of the data collected and/or used as appropriate for each phase of the project. The Project Manager who has responsibility for these summaries will rely on written reports/memoranda documenting the data assessment activities, performance and systems audits, and footnotes identifying qualifications to the data, if any.

Each summary of sampling activities will include a tabulation of the data including:

i) Field duplicate sample results

ii) Maps showing sample locations

iii) An explanation of any sampling conditions or quality assurance problems and their effect on data quality

The GHD QA/QC Officer will prepare quality assurance reports following receipt of all analytical data. These reports will include discussions of the following and their effects on the quality of the data reported:

i) Sample holding times

ii) Laboratory/method blank data

iii) Laboratory control sample recoveries

iv) Internal standard recoveries

v) Field QA/QC data

vi) Pertinent instrument performance per method protocols

vii) Audit results (if performed)

In addition, the quality assurance reports will summarize all quality assurance problems and give a general assessment of quality assurance results versus control criteria for such parameters as accuracy, precision, etc. The quality assurance reports will be forwarded to the Project Manager.

13.1 Specific Routine Procedures Uses to Assess Data Precision, Accuracy, and Completeness

13.1.1 Precision

Precision will be assessed by comparing the analytical results between duplicate analyses. Precision as percent relative difference will be calculated as follows for values significantly greater than the associated detection limit:

$$\text{Precision} = \left| \frac{(D_2 - D_1)}{(D_1 + D_2)/2} \right| \times 100$$

- D_1 = sample result
- D_2 = duplicate sample result

For results near the associated detection limits, precision will be assessed based on the following criteria:

$$\text{Precision} = \left| \text{Original result} - \text{duplicate result} \right| < \text{CRDL}^1$$

13.1.2 Accuracy

Accuracy will be assessed by comparing a set of analytical results to the accepted or "true" values that would be expected. In general, laboratory control sample recoveries will be used to assess accuracy. Accuracy as percent recovery will be calculated as follows:

$$\text{Accuracy} = \frac{A - B}{C} \times 100$$

- A = The analyte determined experimentally from the spike sample
- B = The background level determined by a separate analysis of the unspiked sample
- C = The amount of spike added

13.1.3 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared with the amount that was expected to be obtained under normal conditions.

To be considered complete, the data set must contain all quality control check analyses verifying precision and accuracy for the analytical protocol. In addition, all data are reviewed in terms of stated goals in order to determine if the database is sufficient.

[1] CRDL - Contract Required Detection Limit.

When possible, the percent completeness for each set of samples will be calculated as follows:

$$\text{Completeness} = \frac{\text{usable data obtained}}{\text{total data planned}} \times 100 \text{ percent}$$

13.1.4 Quality Control Exceedances

Procedures discussed previously will be followed for documenting deviations. In the event that a result deviates significantly from method established control limits, this deviation will be noted and its effect on the quality of the remaining data assessed and documented.

14. Preventative Maintenance

This section applies to both field and laboratory equipment. Specific preventive maintenance procedures for field equipment will be consistent with the manufacturer's guidelines. Specific preventive maintenance protocols for laboratory equipment will be consistent with the contract laboratory's SOPs.

All analytical instruments to be used in this project will be serviced by laboratory personnel at regularly scheduled intervals in accordance with the manufacturers' recommendations. Instruments may also be serviced at other times due to failure. Requisite servicing beyond the abilities of laboratory personnel will be performed by the equipment manufacturer or their designated representative.

Routine maintenance of the instruments will be performed as per manufacturers' recommendations. The Laboratory Project Manager is responsible for the preventive maintenance of the instruments.

15. Corrective Action

The need for corrective action may be identified by system or performance audits or by standard quality control procedures. The essential steps in the corrective action system will be:

i) Checking the predetermined limits for data acceptability beyond which corrective action is required

ii) Identifying and defining problems

iii) Assigning responsibility for investigating the problem

iv) Investigating and determining the cause of the problem

v) Determination of a corrective action to eliminate the problem (this may include reanalysis or resampling and analyses)

vi) Assigning and accepting responsibility for implementing the corrective action

vii) Implementing the corrective action and evaluating the effectiveness

viii) Verifying that the corrective action has eliminated the problem

ix) Documenting the corrective action taken

x) Follow-up audits will be performed to verify deficiencies have been corrected

For each measurement system, the Laboratory QA/QC Officer will be responsible for initiating the corrective action, and the Laboratory Project Manager will be responsible for implementing the corrective action.

Table 4.1

Analytical Parameters - Groundwater
Soil Vapor Investigation
Seattle, Washington

	Method	Targeted Quantitation Limit (µg/L)
Volatile Organic Compounds (VOCs)		
1,1,1,2-Tetrachloroethane	SW-846 8260	1.0
1,1,1-Trichloroethane (TCA)	SW-846 8260	1.0
1,1,2,2-Tetrachloroethane	SW-846 8260	1.0
1,1,2-Trichloroethane	SW-846 8260	1.0
1,1-Dichloroethane	SW-846 8260	1.0
1,1-Dichloroethene	SW-846 8260	1.0
1,1-Dichloropropene	SW-846 8260	1.0
1,2,3-Trichlorobenzene	SW-846 8260	1.0
1,2,3-Trichloropropane	SW-846 8260	4.0
1,2,4-Trichlorobenzene	SW-846 8260	1.0
1,2,4-Trimethylbenzene	SW-846 8260	1.0
1,2-Dibromo-3-chloropropane	SW-846 8260	4.0
1,2-Dibromoethane (EDB)	SW-846 8260	1.0
1,2-Dichlorobenzene	SW-846 8260	1.0
1,2-Dichloroethane (EDC)	SW-846 8260	1.0
1,2-Dichloropropane	SW-846 8260	4.0
1,3,5-Trimethylbenzene	SW-846 8260	1.0
1,3-Dichlorobenzene	SW-846 8260	1.0
1,3-Dichloropropane	SW-846 8260	1.0
1,4-Dichlorobenzene	SW-846 8260	1.0
2,2-Dichloropropane	SW-846 8260	4.0
2-Butanone (MEK)	SW-846 8260	5.0
2-Chlorotoluene	SW-846 8260	1.0
2-Hexanone	SW-846 8260	5.0
4-Chlorotoluene	SW-846 8260	1.0
4-Isopropyltoluene	SW-846 8260	1.0
4-Methyl-2-pentanone (MIBK)	SW-846 8260	5.0
Acetone	SW-846 8260	20
Benzene	SW-846 8260	1.0
Bromobenzene	SW-846 8260	1.0
Bromochloromethane	SW-846 8260	1.0
Bromodichloromethane	SW-846 8260	1.0
Bromoform	SW-846 8260	4.0
Bromomethane	SW-846 8260	4.0
Carbon Disulfide	SW-846 8260	1.0
Carbon Tetrachloride	SW-846 8260	1.0
Chlorobenzene	SW-846 8260	1.0
Chloroethane	SW-846 8260	1.0
Chloroform	SW-846 8260	1.0
Chloromethane	SW-846 8260	4.0
cis-1,2-Dichloroethene	SW-846 8260	1.0
cis-1,3-Dichloropropene	SW-846 8260	4.0
Dibromochloromethane	SW-846 8260	1.0
Dibromomethane	SW-846 8260	4.0
Dichlorodifluoromethane	SW-846 8260	1.0
Ethylbenzene	SW-846 8260	1.0
Hexachlorobutadiene	SW-846 8260	1.0
Isopropylbenzene	SW-846 8260	1.0
m,p-Xylenes	SW-846 8260	2.0

Table 4.1

Analytical Parameters - Groundwater
Soil Vapor Investigation
Seattle, Washington

	Method	Targeted Quantitation Limit (µg/L)
VOCs-Continued		
Methylene Chloride	SW-846 8260	4.0
Naphthalene	SW-846 8260	4.0
n-Butylbenzene	SW-846 8260	1.0
n-Propylbenzene	SW-846 8260	1.0
o-Xylene	SW-846 8260	1.0
sec-Butylbenzene	SW-846 8260	1.0
Styrene	SW-846 8260	1.0
tert-Butylbenzene	SW-846 8260	1.0
Tetrachloroethene (PCE)	SW-846 8260	1.0
Toluene	SW-846 8260	1.0
trans-1,2-Dichloroethene	SW-846 8260	1.0
trans-1,3-Dichloropropene	SW-846 8260	4.0
Trichloroethene (TCE)	SW-846 8260	0.4
Trichlorofluoromethane	SW-846 8260	1.0
Vinyl Chloride	SW-846 8260 SIM	0.02
Total Petroleum Hydrocarbons (TPH)		
Gasoline Range Organics	NWTPH-Gx	100
Diesel Range Organics	NWTPH-Dx	400
Oil Range Organics	NWTPH-Dx	400

Notes:

NW - Northwest
SW-846 -Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, 1986, with subsequent revisions
Gx - Gasoline Range Organics
Dx - Diesel Range Organics

Table 4.2

Analytical Parameters - Soil
Soil Vapor Investigation
Seattle, Washington

	Method	Targeted Quantitation Limit (µg/kg)
Volatile Organic Compounds (VOCs)		
1,1,1,2-Tetrachloroethane	SW-846 8260	50.0
1,1,1-Trichloroethane (TCA)	SW-846 8260	50.0
1,1,2,2-Tetrachloroethane	SW-846 8260	50.0
1,1,2-Trichloroethane	SW-846 8260	50.0
1,1-Dichloroethane	SW-846 8260	50.0
1,1-Dichloroethene	SW-846 8260	50.0
1,1-Dichloropropene	SW-846 8260	50.0
1,2,3-Trichlorobenzene	SW-846 8260	50.0
1,2,3-Trichloropropane	SW-846 8260	200
1,2,4-Trichlorobenzene	SW-846 8260	50.0
1,2,4-Trimethylbenzene	SW-846 8260	50.0
1,2-Dibromo-3-chloropropane	SW-846 8260	500
1,2-Dibromoethane (EDB)	SW-846 8260	50.0
1,2-Dichlorobenzene	SW-846 8260	50.0
1,2-Dichloroethane (EDC)	SW-846 8260	50.0
1,2-Dichloropropane	SW-846 8260	50.0
1,3,5-Trimethylbenzene	SW-846 8260	50.0
1,3-Dichlorobenzene	SW-846 8260	50.0
1,3-Dichloropropane	SW-846 8260	50.0
1,4-Dichlorobenzene	SW-846 8260	50.0
2,2-Dichloropropane	SW-846 8260	200
2-Butanone (MEK)	SW-846 8260	250
2-Chlorotoluene	SW-846 8260	50.0
2-Hexanone	SW-846 8260	250
4-Chlorotoluene	SW-846 8260	50.0
4-Isopropyltoluene	SW-846 8260	50.0
4-Methyl-2-pentanone (MIBK)	SW-846 8260	250
Acetone	SW-846 8260	1000
Benzene	SW-846 8260	20.0
Bromobenzene	SW-846 8260	50.0
Bromochloromethane	SW-846 8260	50.0
Bromodichloromethane	SW-846 8260	50.0
Bromoform	SW-846 8260	200
Bromomethane	SW-846 8260	500
Carbon Disulfide	SW-846 8260	50.0
Carbon Tetrachloride	SW-846 8260	50.0
Chlorobenzene	SW-846 8260	50.0
Chloroethane	SW-846 8260	500
Chloroform	SW-846 8260	50.0
Chloromethane	SW-846 8260	200
cis-1,2-Dichloroethene	SW-846 8260	50.0
cis-1,3-Dichloropropene	SW-846 8260	50.0
Dibromochloromethane	SW-846 8260	200
Dibromomethane	SW-846 8260	50.0
Dichlorodifluoromethane	SW-846 8260	200
Ethylbenzene	SW-846 8260	50.0
Hexachlorobutadiene	SW-846 8260	250

Table 4.2

Analytical Parameters - Soil
Soil Vapor Investigation
Seattle, Washington

	Method	Targeted Quantitation Limit (µg/kg)
VOCs-Continued		
Isopropylbenzene	SW-846 8260	50.0
m,p-Xylenes	SW-846 8260	100
Methylene Chloride	SW-846 8260	200
Naphthalene	SW-846 8260	200
n-Butylbenzene	SW-846 8260	50.0
n-Propylbenzene	SW-846 8260	50.0
o-Xylene	SW-846 8260	50.0
sec-Butylbenzene	SW-846 8260	50.0
Styrene	SW-846 8260	50.0
tert-Butylbenzene	SW-846 8260	50.0
Tetrachloroethene (PCE)	SW-846 8260	50.0
Toluene	SW-846 8260	50.0
trans-1,2-Dichloroethene	SW-846 8260	50.0
trans-1,3-Dichloropropene	SW-846 8260	200
Trichloroethene (TCE)	SW-846 8260	30.0
Trichlorofluoromethane	SW-846 8260	200
Vinyl Chloride	SW-846 8260	20.0
Total Petroleum Hydrocarbons (TPH)		
Gasoline Range Organics	NWTPH-Gx	5000
Diesel Range Organics	NWTPH-Dx	15000
Oil Range Organics	NWTPH-Dx	15000
Physical Properties		
Moisture Content	ASTM D2216	-
Porosity	ASTM D2937	-
Organic Carbon Fraction	ASTM D2974	-
Grain-Size Distribution by Sieve	ASTM D422	-
Dry Bulk Soil Density	ASTM D2937	-

Notes:

NW - Northwest
SW-846 -Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, 1986, with subsequent revisions
ASTM - American Society for Testing and Materials
Gx - Gasoline Range Organics
Dx - Diesel Range Organics

Table 4.3

Analytical Parameters - Vapor
Soil Vapor Investigation
Seattle, Washington

	Method	Targeted Quantitation Limit ($\mu g/m^3$)
Volatile Organic Compounds (VOCs)		
1,1,1-Trichloroethane	TO-15	1.25
1,1,2,2-Tetrachloroethane	TO-15	1.25
1,1,2-Trichloroethane	TO-15	1.25
1,1-Dichloroethane	TO-15	1.25
1,1-Dichloroethene	TO-15	1.25
1,2,4-Trichlorobenzene	TO-15	1.25
1,2,4-Trimethylbenzene	TO-15	1.25
1,2-Dibromo-3-chloropropane	TO-15	1.25
1,2-Dibromoethane	TO-15	1.25
1,2-Dichloro-1,1,2,2-tetrafluoroethane (CFC 114)	TO-15	1.25
1,2-Dichlorobenzene	TO-15	1.25
1,2-Dichloroethane	TO-15	1.25
1,2-Dichloropropane	TO-15	1.25
1,3,5-Trimethylbenzene	TO-15	1.25
1,3-Butadiene	TO-15	1.25
1,3-Dichlorobenzene	TO-15	1.25
1,4-Dichlorobenzene	TO-15	1.25
1,4-Dioxane	TO-15	1.25
2-Butanone (MEK)	TO-15	13
2-Hexanone	TO-15	1.25
2-Propanol (Isopropyl Alcohol)	TO-15	2.5
3-Chloro-1-propene (Allyl Chloride)	TO-15	1.25
4-Ethyltoluene	TO-15	1.25
4-Methyl-2-pentanone	TO-15	1.25
Acetone	TO-15	12.5
Acetonitrile	TO-15	1.25
Acrolein	TO-15	5
Acrylonitrile	TO-15	1.25
alpha-Pinene	TO-15	1.25
Benzene	TO-15	1.25
Benzyl Chloride	TO-15	1.25
Bromodichloromethane	TO-15	1.25
Bromoform	TO-15	1.25
Bromomethane	TO-15	1.25
Carbon Disulfide	TO-15	13
Carbon Tetrachloride	TO-15	1.25
Chlorobenzene	TO-15	1.25
Chloroethane	TO-15	1.25
Chloroform	TO-15	1.25
Chloromethane	TO-15	1.25
cis-1,2-Dichloroethene	TO-15	1.25
cis-1,3-Dichloropropene	TO-15	1.25
Cumene	TO-15	1.25
Cyclohexane	TO-15	2.5
Dibromochloromethane	TO-15	1.25
Dichlorodifluoromethane (CFC 12)	TO-15	1.25
d-Limonene	TO-15	1.25

Table 4.3

Analytical Parameters - Vapor
Soil Vapor Investigation
Seattle, Washington

	Method	Targeted Quantitation Limit ($\mu g/m^3$)
VOCs-Continued		
Ethanol	TO-15	12.5
Ethyl Acetate	TO-15	2.5
Ethylbenzene	TO-15	1.25
Hexachlorobutadiene	TO-15	1.25
m,p-Xylenes	TO-15	2.5
Methyl Methacrylate	TO-15	2.5
Methyl tert-Butyl Ether	TO-15	1.25
Methylene Chloride	TO-15	1.25
Naphthalene	TO-15	1.25
n-Butyl Acetate	TO-15	1.25
n-Heptane	TO-15	1.25
n-Hexane	TO-15	1.25
n-Nonane	TO-15	1.25
n-Octane	TO-15	1.25
n-Propylbenzene	TO-15	1.25
o-Xylene	TO-15	1.25
Propene	TO-15	1.25
Styrene	TO-15	1.25
Tetrachloroethene	TO-15	1.25
Tetrahydrofuran (THF)	TO-15	1.25
Toluene	TO-15	1.25
trans-1,2-Dichloroethene	TO-15	1.25
trans-1,3-Dichloropropene	TO-15	1.25
Trichloroethene	TO-15	1.25
Trichlorofluoromethane (CFC 11)	TO-15	1.25
Trichlorotrifluoroethane (CFC 113)	TO-15	1.25
Vinyl Acetate	TO-15	12.5
Vinyl Chloride	TO-15	1.25
Total Petroleum Products (TPH)		
C5-C8 Aliphatics	MA-APH	20
C9-C12 Aliphatics	MA-APH	10
C9-C10 Aromatics	MA-APH	2.5
Fixed Gases		
Oxygen	ASTM D1946	0.10% v/v
Carbon Dioxide	ASTM D1946	0.10% v/v
Methane	ASTM D1946	0.10% v/v
Helium	EPA 3C Mod	25 ppmV

Notes:

MA-APH - Massachusetts Air Phase Hydrocarbons
ASTM - American Society for Testing and Materials
TO-15 - Determination of Volatile Organic Compounds in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry
EPA - Environmental Protection Agency

Table 4.4

Sampling and Analysis Summary
Soil Vapor Investigation
Seattle, Washington

Matrix	Analytical Parameter	Analytical Method	Estimated Number of Samples	Field Duplicates	Trip Blanks	MS/MSD/Dup
Groundwater						
	TCL VOCs	SW-846-8260 / 8260 SIM	7	1	1 / day	1/1/0
	TPH-Gx/Dx/Ox	NWTPH	7	1	-	1/1/0
Soil						
	TCL VOCs	SW-846-8260	16	1	-	1/1/0
	TPH-Gx/Dx/Ox	NWTPH	16	1	-	1/1/0
	Moisture Content	ASTM D2216	8	-	-	-
	Porosity	ASTM D2937	8	-	-	-
	Organic Carbon Fraction	ASTM D2974	8	-	-	-
	Grain-Size Distribution by Sieve	ASTM D422	8	-	-	-
	Dry Bulk Soil Density	ASTM D2937	8	-	-	-
Vapor						
	TCL VOCs	TO-15	16	1	1*	1/1/0
	TPH	MA-APH	16	1	1*	1/1/0
	Fixed Gases	ASTM D1946	16	1	1*	0/0/1
	Helium	EPA 3C Mod	16	1	-	0/0/1

Notes:

Dup - Duplicate
MS - Matrix Spike/Matrix Spike Duplicate
TCL - Target Compound List
TPH - Total Petroleum Hydrocarbons
VOCs - Volatile Organic Compounds
Gx - Gasoline Range Organics
Dx - Diesel Range Organics
Ox - Oil Range Organics
* - Ambient Air
- - Not applicable
NW - Northwest
MA-APH - Massachusetts Air Phase Hydrocarbons
ASTM - American Society for Testing and Materials
TO-15 - Determination of Volatile Organic Compounds in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry
EPA - Environmental Protection Agency
SW-846 - Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition, 1986, with subsequent revisions

Table 7.1

Sample Container, Preservation, and Holding Time Periods
Soil Vapor Investigation
Seattle, Washington

Analyses	Sample Containers	Preservation	Maximum Holding Time	Notes
Groundwater				
TCL VOCs	Three 40-mL glass vials Teflon-lined septum	pH <2, HCl Cool <6°C	14 days from collection to analysis	Fill completely with no head space
TPH-Gx	Three 40-mL glass vials Teflon-lined septum	pH <2, HCl Cool <6°C	14 days from collection to analysis	Fill completely with no head space
TPH-Dx/Ox	Two 250-mL Amber	pH <2, HCl Cool <6°C	14 days to extraction, 40 days to analysis	Fill completely with no head space
Soil				
TCL VOCs	Two 40-mL glass vials with methanol	Cool <6°C	48 hours to preservation, 14 days to analysis	Fill per instructions
TPH-Gx	Two 40-mL glass vials with methanol	Cool <6°C	48 hours to preservation, 14 days to analysis	Fill per instructions
TPH-Dx/Ox	One 4-oz. glass jar	Cool <6°C	14 days to extraction, 40 days to analysis	
Physical Parameters	Macrocore liner	Cool <6°C	-	
Vapor				
TCL VOCs	6-Liter stainless steel canister	none	30 days	Fill to a residual vacuum of 2-10" Hg
TPH	*		28 days	
Fixed Gases	*		30 days	
Helium	*		30 days	

Notes:

TCL - Target Compound List
VOCs - Volatile Organic Compounds
TPH - Total Petroleum Hydrocarbons
Gx - Gasoline Range Organics
Dx - Diesel Range Organics
Ox - Oil Range Organics
HCl - Hydrochloric Acid
Hg - Mercury
* - All analyses performed from canister
- - Not applicable

Table 10.1

Laboratory Reporting Deliverables
Soil Vapor Investigation
Seattle, Washington

A detailed report narrative should accompany each submission, summarizing the contents and results.

A. Chain of Custody Documentation and Detailed Narrative[(1)]

B. Sample Information
   1. Date collected
   2. Date extracted or digested
   3. Date analyzed
   4. Analytical method and reference

C. Data (including all raw data and Contract Laboratory Program [CLP]-like summary forms)
   1. Samples
   2. Laboratory duplicates[(2)]
   3. Method blanks
   4. Spikes, spike duplicates[(2) (3)]
   5. Surrogate recoveries[(2)]
   6. Internal standard recoveries
   7. Calibration
   8. Any other applicable quality control (QC) data (i.e., serial dilution)
   9. Tentatively Identified Compounds (TICs) (if applicable)

D. Miscellaneous
   1. Method detection limits and/or instrument detection limits
   2. Percent solids (where applicable)
   3. Metals run logs
   4. Standard preparation logs
   5. Sample preparation logs

All sample data and its corresponding quality assurance/quality control (QA/QC) data shall be maintained accessible to GHD in electronic format.

Notes:

(1) - Any QC outliers must be addressed and corrective action taken must be specified

(2) - Laboratory must specify applicable control limits for all QC sample results

(3) - A blank spike must be prepared and analyzed with each sample batch

Attachments

Attachment A
Standard Operating Procedures

Pace Analytical Services, LLC
1700 Elm Street SE, Suite 200
Minneapolis, MN 55414

Phone: 612-607-1700
Fax: 612-607-6444

STANDARD OPERATING PROCEDURE

ANALYSIS OF VOLATILE ORGANIC COMPOUNDS BY GC/MS

Reference Methods: SW846 Method 8260B

Local SOP Number:	S-MN-O-521-rev.35
Effective Date:	Date of Final Signature
Supersedes:	S-MN-O-521-rev.34

APPROVALS

Laboratory General Manager — Date: 12 Jul 2018

Laboratory Quality Manager — Date: 12 Jul 2018

PERIODIC REVIEW

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

Signature	Title	Date

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TABLE OF CONTENTS

SECTION **PAGE**

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to define the process for the determination of volatile organic compounds by gas chromatography/mass spectrometry (GC/MS), capillary column technique per SW-846 method 8260B**.**

2. Summary of Method

2.1. The volatile organic compounds are introduced into the gas chromatograph by the purge-and trap method. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and back flushed with helium to desorb trapped sample components. The analytes are directly desorbed onto a narrow bore capillary column connected to a split/splitless injection port. The column is temperature programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph.

2.2. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is quantitated by relating the MS response for an appropriate selected ion produced by that compound to the MS response for an appropriately selected ion produced by an internal standard.

3. Scope and Application

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

3.2. **Parameters**: This SOP applies to compounds listed in Attachment I. Additional compounds may be analyzed if all quality control criteria are met.

3.3. Method 8260B can be used to quantitate most volatile organic compounds that have boiling points below 200° C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately two to ten times higher because of poor purging efficiency. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitrites, acetates, acrylates, ethers, and sulfides.

3.4. Method 8260B is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

4. Applicable Matrices

4.1. This SOP is applicable to a variety of matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, surface water, aqueous sludges, soils, and sediments.

5. Limits of Detection and Quantitation

5.1. All current MDLs and LOQs are listed in the LIMS and are available by request from the Quality Manager.

5.2. Reporting Limits will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

6. Interferences

6.1. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such

materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should investigate the source of contamination and correct it. Subtracting blank values from sample results is not permitted. If reporting values not corrected for blanks results in what the laboratory feels is a false positive for a sample, this should be fully explained in text accompanying the uncorrected data.

6.2. Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing of the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After analysis of a sample containing high concentrations of volatile organic compounds, one or more method blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high concentrations of compounds being determined, it may be necessary to wash the purging device with methanol, rinse it with organic-free reagent water, and then dry the purging device in an oven less than 120°C. In extreme situations, the whole purge and trap device may require dismantling and cleaning, typically a methanol back flush followed by a DI water back flush. Screening the sample prior to analysis is recommended to prevent system contamination. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique using a flame ionization detector or by analyzing the sample at a dilution by purge and trap GC/MS.

6.3. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank is prepared using organic-free water (or pre-tested, boiled and/or purged DI water) and carried through the sampling and handling protocol or pre tested, boiled, deionized water can serve as a check on such contamination. Trip blanks may also be purchased premade, refer to the Bottle Preparation SOP, S-MN-C-003, or equivalent replacement.

6.4. Holding blanks consisting of VOA vials of DI water or methanol are placed in the refrigerators and freezers used for the storage of samples for volatile analysis. These blank samples are removed every two weeks and analyzed for the target analytes to determine if cross-contamination has occurred during sample storage.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Table 7.1 Sample Collection, Preservation and Storage.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	3 VOA vials, approximately 42 mL total volume when capped with no headspace (no headspace is considered less than 6 mm bubble present in container	Acidified with 1:1 hydrochloric acid (HCl) to pH<2; no headspace	<6°C, but above freezing	Must be analyzed within 14 days of collection when properly preserved; 7 days if the pH is >2
Aqueous for Acrolein and Acrylonitrile	3 VOA vials, approximately 42 mL total volume when capped with no headspace (no headspace is considered less than 6 mm bubble present in container	Adjust pH to pH 4-5	<6°C, but above freezing	Must be analyzed within 14 days of collection when properly preserved; 3 days in no pH adjustment is made per 40 CFR Part 136 guidance

Solids – Low level by 5035	2 unpreserved tared 40 mL vial with stirbar and 5 mL DI water	DI water	<6°C, but above freezing	Must be frozen within 48 hours of collection to -10 to -20 °C and analyzed within 14 days of collection
Solids – Medium level by 5035	2 Tared 40 mL vial or wide mouth jar – 25 g capacity Encore, or similar approved sample container and storage device (Terracore)	Methanol	<6°C, but above freezing	Must be analyzed within 14 days of collection when properly preserved
TCLP/SPLP Leachate	2 VOA vials, approximately 42 mL total volume when capped with no headspace (no headspace is considered less than 5-6 mm bubble present in container	The leachate solution provides a pH generally <2 so no additional chemical preservative is added	<6°C, but above freezing	Must be analyzed within 14 days of the end of the leaching process to analysis

7.2. Acceptable sample collection options for low level 5035 soil samples are listed below:

7.2.1. 40mL tared vial preserved with Sodium Bisulfate. Note- Sodium Bisulfate preserved vials are not recommended or generally supplied by Pace. The reason why sodium bisulfate is not recommended is due to the possibility of ketones contamination/formation. Depending on the soil matrix, the sodium bisulfate can react to the soil to form ketones. Therefore if the client chooses to use sodium bisulfate as the preservative there may be ketones detections. Also sodium bisulfate is destructive to the autosamplers and concentrators causing additional maintenance and down time.

7.2.2. 5g capacity Encore or similar approved sample collection and storage device (i.e. Terracore).

7.2.3. Method criteria states that the sample weight should be 5 ± 0.5g, but due to field sampling the weights may vary. Pace will qualify samples that are received with greater than 7.5 grams of sample. There may also be times due to matrix, such as an ash, that weights lower than 5 grams result in the lab not being able to perform an adequate purge. Pace will notify the clients of the matrix difficulties, analyze and qualify accordingly.

7.3. Samples collected in Encore or similar devices must be extruded within 48 hours of collection. Alternatively, samples may be frozen. The extrusion time and date must be recorded in the extrusion logbook.

7.3.1. For low-level soil – extrude the sample into a tared 40mL vial containing 5mL of organic free reagent water and a clean stir bar. Record the weight in the extrusion logbook. Record the date and time of extrusion in the extrusion logbook. Cap the vial and freeze at -10 to -20oC until analysis.

7.3.2. For medium-level soils – extrude the sample into a tared 40mL vial. Record the weight in the extrusion logbook. Record the date and time of extrusion in the extrusion logbook. Add the appropriate ratio of methanol to the weight of the soil (e.g. 10mL methanol to 10g of sample) and cap.

7.3.3. If a client is collecting and freezing in the field, Pace assumes that the samples are frozen within the 48 hour requirement if they are received frozen if no associated paperwork is received indicating otherwise. The laboratory will not qualify the data if the samples are received frozen.\

7.3.3.1. If the samples were anticipated to be received frozen, and are received in a manner indicating that the samples were not completely frozen or thawed on transport, sample receiving will mark the containers received thawed with an "X" on the cap to alert the laboratory.

7.3.3.2. If there is volume available that was received frozen, that container should be used for analysis. If there is no frozen volume available and the lab must used a "X" container for analysis, the lab must qualify the data as being performed by a container that had not been completely frozen.

7.4. Multiple states allow for packed jars for soil analysis. For samples that are received in a pack jar, there may be client specific requirements that direct the subsampling and preserving within 48 hours as directed by Method 5035.

7.4.1. If the samples were not preserved within 48 hours, document the information on the associated preparation logbook. Qualify the data according to client specific instructions as necessary.

7.4.2. A packed jar will be considered to contain headspace if the soil falls below the threads of the vial. If there is headspace, the data will be qualified to indicate that analysis was conducted on a sample that contained headspace.

8. Definitions

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

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

9.1. Table 9.1 Equipment and Supplies.

Supply	Description	Vendor/ Item # / Description
Autosampler	Varian Archon 5100 and EST Archon 8100, Centurion w/s (or equivalent), or Atomx	Varian, Tekmar or Centurion
Sample Concentrator	EST Encon Evolution(EV) Concentrator, Tekmar Atomx, Tekmar (Lab Sample Concentrator) LSC 3100, LSC 3000, OI analytical Eclipse or equivalent	Encon, OI or Tekmar
Purging Chamber	The purging chamber is designed to accept 5mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap should be minimized. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3mm at the origin. The purge gas must be introduced no more than 5mm from the base of the water column	Encon,Tekmar, OI analytical or equivalent replacement
Traps	Trap Packing - A variety of traps are available from manufacturers. Any of these traps may be used if the trap packing materials do not introduce contaminants into the analysis and the data generated using the trap meets the initial and continuing calibration technical acceptance criteria of this method. Some traps used include, but are not limited to a tenax/silica gel/carbon trap, tenax/silica gel/carbon/OV-1 trap, and a Vocarb 3000 trap.	E7300-K03, EVO K trap E07300-L03, EVO MoRT trap Supelco 24920-u, Tekmar K traps for 3000/3100 Supelco 24910-U, Tekmar A traps for 3000/3100 14-9908-403,#9 (U-shaped) 14-9908-003, #9 (Straight Trap) straight trap H

Desorber	EST EV, Tekmar LSC-3100, LSC 3000 or equivalent should be capable of rapidly heating the trap to the manufacturer's recommended temperature for desorption, typically 180°C to 260°C, depending on the trap chosen	Encon, OI, Tekmar, or equivalent replacement
Sample Heater	Should be capable of maintaining the purging chamber at 40°	Varian, Tekmar, Centurion, OI or equivalent replacement
Gas Chromatograph	An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection (Hewlett Packard HP 6890 or equivalent)	Agilent/Hewlett Packard, or equivalent replacement
Column	20 m x 0.18 mm ID x 1.0 µm film thickness capillary column	RestekVMS-Rtx, or equivalent replacement
Mass Spectrometer	Capable of 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 Bromofluorobenzene (BFB) which meets all of the criteria in Table III when 5-50 ng of the GC/MS tuning standard (BFB) are directly injected onto the column. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC (HP5973MSD or equivalent)	Agilent/Hewlett Packard, or equivalent replacement
Transfer Line	GC/MS interface - The GC is interfaced to the MS with an all glass enrichment device and an all glass transfer line. Any GC-to-MS interface that gives acceptable calibration points at 50ng or less per injection for each of the analytes and achieves all acceptable performance criteria may be used. If a 0.18-0.32 mm ID capillary column is used, it is positioned directly into the ion source and this GC/MS interface acts only as a heated connection, not as an enrichment device	Agilent/Hewlett Packard, or equivalent replacement
Shaker Table	A shaker table is used to mix samples thoroughly prior to being analyzed on the instrument.	Precision Scientific 360P Orbital Shaker. CAT#67127, or equivalent replacement
Data System	A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.	Hewlett-Packard Chemserver
Data Processing Software		Target 4.1, or equivalent replacement

Data Package and Review Software	Compiles pdf images of all the data to be available for package generation and secondary review	Gandalf, see master software list for revision
Data Reporting Software	Laboratory information management system (LIMS)	Horizon, see master software list for revision
Microsyringes	10 , 25, 50, 100, 250, 500, and 1000µL	Hamilton, or equivalent replacement
Syringes	5, 10, 25mL, 50 mL or gas-tight with shutoff valve	Hamilton, or equivalent replacement
Eppendorf Pipettor	1000µL	Eppendorf, or equivalent replacement
Balance	Analytical, 0.0001g, and top-loading, 0.1g	
2mL Screw Top Vials	Clear glass vials, 2mL with Teflon-lined screw cap	Fisher Scientific C40131500 or equivalent replacement
Disposable pipettes	Glass pasteur pipettes	Fisher Scientific 13-678-31J or equivalent replacement
Volumetric Flasks	Class A - 5mL, 10mL, 25mL, 50mL, and 100mL, 200mL, 250mL, and 1000mL with ground-glass stoppers	Fisher Scientific or equivalent replacement
Spatula	Stainless steel	Fisher Scientific equivalent replacement
VOA vials	40 mL VOA Vials actual volume without headspace = 42 mL	C&G Unpreserved Vials NC9879693 or equivalent replacement

10. Reagents and Standards

10.1 Table 10.1 Reagents and Standards.

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Organic-free Water (DI)	De-ionized water, may be boiled and/or purged to further remove volatile contaminants	Verify that background levels of volatile compounds are acceptable by analysis
Methanol (MeOH)	CH_3OH - Fisher Purge and Trap grade or equivalent, demonstrated to be free of analytes. Store apart from other solvents	Fisher Scientific A453-1 or equivalent replacement
Stock Standard	Stock solutions are typically purchased as certified solutions. Multiple stock standards can be combined (diluted) to yield one working standard. 1000-40,000mg/L	O_2Si - 121369-02-02 (8260 Gases) O_2Si - 020986-02-02 (Freon 21) O_2Si - 121370-02-02 (Custom Mix 98-1370) O_2Si - 125875-05 (Reactive 5-81) or equivalent
Surrogate Standard	10,000mg/L	O_2Si -120330-03-P (8260 IS/SS Soln)
Initial Calibration Verification Stock Standard	1000-40,000mg/L	O_2Si - 121369-02-02-SS (8260 Gases SS) O_2Si - 020986-02-02-SS (Freon 21 SS) O_2Si - 121370-02-02-SS (Custom Mix 98-1370SS) O_2Si - 125875-05-SS (Reactive 45-81SS) or equivalent
Internal Stock Standard	10,000mg/L; 10,000-100,000mg/L	O_2Si -120330-03-P (8260 IS/SS Soln); Chem Service Inc. - SP-89304710CSZ (1,4-dioxane d8 and acetone d6)
Tuning Standard	10,000mg/L	O_2Si -120330-03-P (8260 IS/SS Soln)
Anti-Foaming Agent	Dow Corning 1520-US Antifoam (or equivalent replacement). Add 2g to 42 mL of DI water and mix vigorously. The solution must be gently shaken solution	Dow Corning 1520-US

	prior to use. If anti-foam is used for samples, injection 100-200uL of anti-foam solution into the vial	

10.2 Working Standard Dilutions and Concentrations

Standard	Standard(s) Amount	Solvent	Solvent Diluent Diluent Volume	Final Total Final Volume	Final Concentration
Intermediate Tune Solution	500 µL	Methanol	100 mL	50 µg/mL	Intermediate Tune Solution
Tune	5 µL	Water	5mL	50 µg/L	Tune
Calibration Working Standard	0.5mL of 1000mg/L-40,000mg/L	Methanol	9.5mL methanol	10mL	50-2000 µg/mL(nominal conc 100ug.mL)
Calibration Std 1	0.5 µL	Methanol	249.999 water	250 mL	0.2 µg/L
Calibration Std 2	1.0 µL	Methanol	249.9995 water	250 mL	0.4 µg/L
Calibration Std 3	1.0 µL	Methanol	99.999 water	100 mL	1 µg/L
Calibration Std 4	4.0 µL	Methanol	99.996 water	100 mL	4 µg/L
Calibration Std 5	10.0 µL	Methanol	99.99 water	100 mL	10 µg/L
Calibration Std 6	20.0 µL	Methanol	99.98 water	100 mL	20 µg/L
Calibration Std 7	50.0 µL	Methanol	99.95 water	100 mL	50 µg/L
Calibration Std 8	100.0 µL	Methanol	99.90 water	100 mL	100 µg/L
Calibration Std 9	250.0 µL	Methanol	99.75 water	100 mL	250 µg/L
Surrogate Working Standard for Archon	0.5mL of 10,000mg/L	Methanol	19.5mL methanol	20mL	250 µg/mL
Surrogate Working Standard for Centurion	0.5mL of 10,000mg/L	Methanol	99.5mLmethanol	100mL	50 µg/mL
Internal Standard Working Standard for Archon	0.5mL of 10,000mg/L; 0.5mL of 10,000 to 100,000mg/L	Methanol	19.5mL methanol	20mL	250 µg/mL (1,4-dioxane-d8 is at 5000 µg/mL)
Internal Standard Working Standard for Centurion	0.5mL of 10,000mg/L; 0.5mL of 10,000 to 100,000mg/L	Methanol	99.5mLmethanol	100mL	50 µg/mL (1,4-dioxane-d8 is at 1000 µg/mL)
Continuing Calibration Verification Standard at 50ppb	100uL of working std	Water	199.9mL of water	200mL	50ug/mL
Continuing Calibration Verification Standard at 20ppb	50uL of working std	Water	249.95mL of water	250mL	20ug/mL

10.2.1 Calibration standards for SIM/SCAN simultaneous acquisition are prepared by diluting calibration std 5 (10ug/L final concentration-see above) with an appropriate volume of organic free DI water. Dilutions are performed in 100mL volumetric flasks and diluted to a final concentration of 0.005ug/L, 0.01ug/L, 0.05ug/L, and 0.1ug/L. For SIM/SCAN analysis the calibration curve is named as calibration std 1 through calibration std 13 beginning with the lowest concentration.

10.3 All standards, blanks, spikes, and samples must be analyzed using the same conditions. A set of at least five calibration standards containing the method analytes and surrogates are needed (six standards are necessary for quadratic curve fits). One calibration standard should contain each analyte at a concentration at or below the reporting limit for that compound; the other calibration standards should contain analytes at concentration that define the range of the method. To prepare a calibration standard, add an appropriate volume of standard solution to organic-free reagent water in a volumetric flask. Using a microsyringe, rapidly inject the standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times. Transfer the standard to a 40 mL VOA vial and load into the Autosampler. If ICAL or CCVs are not used immediately they must be stored at 0 to 6 degrees Celsius in a cooler which does not house samples for up to one day from the day they were made.

10.4 The following is an example of standard preparation for an initial calibration. Standard preparation is determined by client and project requirements. Unless a reporting limit of 0.2µg/L or lower is required, the low standard will typically be prepared at 0.4µg/L. A "soil" curve to reflect the chromatography conditions of medium level soils (1:50 ratio of MeOH:water) is prepared by adding 2 mL of methanol into the calibration standards and reducing the volume of reagent water accordingly. Additional levels may be performed.

10.5 For the centurions autosamplers, a 5 µL aliquot of the intermediate tune solution is added to the sample loop that is transferred to the sparge tube, at this point it is a 5 mL solution at a concentration of 50 µg/L on column. The method criteria of 5-50 ng is met as the split ratio is set at 30:1 to 50:1 depending on instrument resulting in >5 ng at the mass spectrometer.

11. Calibration and Standardization

11.1. Table 11.1 Calibration and Standardization.

Calibration Metric	Parameter / Frequency	Criteria	Comments
Tune (BFB)	Every 12 hours	See below in 11.2	If the tune criteria is not met, evaluate the standard preparation. Perform any vendor recommended maintenance including hardware tune using perfluorotirbutylamine (PFTBA). The tune must pass prior to any analysis being conducted.
Calibration Curve Fit	Average Response Factor Linear Regression Non-linear Regression(quadratic)	% RSD: 30% for CCCs, 15% for all others $r \geq 0.995$ $COD \geq 0.99$ *See 11.3 and 11.4 for CCCs and SPCCs*	If not met, try non-linear regression fit. If still not met, remake standards and recalibrate and verify before sample analysis.
Second Source Verification Standard (ICV)	after each initial calibration	CCV criteria + 10% unless otherwise specified in a QAPP	If the requirements for ICV are not met, verify the standard preparation and if there are any apparent issues with the initial analysis. Reanalyze one more time. Only two injections of the same standard are permitted back to back prior to recalibrating the instrument. May be used as a CCV if CCV requirements are met.

			Secondary source standard is also here-in referred to as non-calibration source standard to note that although the primary and secondary source standards are comparable in concentration and used interchangeably, The calibration is prepared from a separate source than is used for ICV, CCV, and QC spiked samples. (i.e. A calibration curve may be prepped with secondary source so long as the affiliated ICV,CCV, LCS,LCSD, MS, and MSD are spiked using the primary (non-calibration) source.)
Reporting Limit Verification	Initially evaluated from the Ical levels and every 30 days after or until next Ical is necessary	The reporting limit must be ± 40% of the true value for MN originating samples	Requantitate the reporting limit standard in the Ical once the linear regression has been established to verify the recoveries. If the criteria is not met, review for any calculation errors. Evaluate for recalibration. Depending on data quality objectives, the reporting limit may be raised to the next passing Ical level.
Continuing Calibration Verification (CCV)	Prior to the analysis of any samples and be verified every 12 hours following the tune Prepared using non-calibration source standard	% Diff ±20% for CCCs, and ±40% for non-CCCs If a CCV is evaluated using a sublist that does not include all the CCCs, CCC criteria applies to all the compounds in the list. Client, QAPP, or state requirements may supersede this requirement.	If the requirements for CCV are not met, verify the standard preparation and if there are any apparent issues with the initial analysis. Reanalyze one more time. Only two injections of the same standard are permitted back to back prior to recalibrating the instrument.
Internal Standards	All analytical runs	Retention time must be ±30 seconds of any internal standard from the ccv; the response factor must be within -50% to 200%. Client, QAPP, or state requirements may supersede this requirement.	The chromatographic system must be inspected for malfunctions and corrections must be made.

11.2. Each GC/MS system must be hardware-tuned using perfluorotributylamine (PFTBA) and must also meet the criteria below for a 5-50ng injection of 4-bromofluorobenzene. Analyses must not begin until these criteria are met.

BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
95	Base Peak, 100% relative abundance
50	15.00 - 40.00% of m/z 95
75	30.00 - 60.00% of m/z 95
96	5.00 - 9.00% of m/z 95
173	Less than 2.00% of m/z 174
174	50.00-120% of m/z 95
175	5.00 - 9.00% of m/z 174
176	95.00 to 101.00% of m/z 174
177	5.00 - 9.00% of m/z 176

Note: All ion abundance must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent.

The mass spectrum of BFB should be acquired in the following manner. Three scan (the peak apex and the scans immediately preceding and following the apex) and acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of BFB. Part of the BFB peak must not be background subtracted

11.3. CCCs include the list below:

1,1-Dichloroethene	1,2-Dichloropropane
Chloroform	Toluene
Ethylbenzene	Vinyl Chloride
NOTE: Additional CCCs may be specified on a client and project-specific basis. If a sublist is analyzed all analytes are treated as CCCs	

11.4. System Performance Check Compounds (SPCCs) are checked for a minimum average response factor. The SPCCs and the minimum response is listed below:

Compound	**Minimum Response**
Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachlorethane	0.30

11.5. For water and low level soil analysis, the CCV and LCS/LCSD solutions are the same solution (prepared at the same, using the same standards, etc.). The CCV and LCS/LCSD analyses are interchangeable and can be used for both sample types (the CCV can also be used as the LCS and the LCS can also be used as the CCV) provided that 2 CCV's didn't already fail in a row (which would trigger an initial calibration). When these analytical runs are used as the same file, they should be named as 2 separate files to distinguish the sample types for reporting the appropriate reports and so that there is a unique file name associated with each sample type.

11.6. For medium level soils, LCS/LCSD's are not interchangeable with the CCV's in the run sequences as the LCS/LCSD's are prepared and extracted with the associated sample on the day of preparation while the CCV's and initial calibration solutions are prepared by using a ratio of 1 mL methanol into 50 mL of DI water (to matrix match the calibrations to the sample matrix) and are not extracted.

11.7. INITIAL CALIBRATION VERFICATION (ICV)

11.7.1. To ensure internal standard recoveries from samples that run after the Ical under the same folder go off the Ical and not the ICV, process the ICV as a sample. To see if the ICV meets

passing requirements pull the ICV file into a batch.b along with the method and requant the ICV as a continuing calibration.

11.8. CONTINUING CALIBRATION VERIFICATION (CCV)

11.8.1. The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition.

11.8.2. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration, the analytical system must be inspected for malfunctions and corrections must be made.

11.8.3. If the EICP area for any of the internal standards changes by a factor of two, (-50% to +100%) from the last daily calibration standard check, the system must be inspected for malfunctions and corrections must be made.

12. Procedure

12.1 Water/Leachate Sample Analysis.

12.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Screening can be accomplished by using a headspace GC PID or by analyzing the sample at a dilution by GC/MS. When available, historical data may be used to perform dilutions prior to analysis.

12.1.2 BFB tuning criteria and daily GC/MS calibration criteria must be met before analyzing samples (see 11.2)

12.1.2.1 The BFB and calibration verification standard may be combined into a single analysis as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

12.1.3 Sample vials are loaded onto the autosampler. All leachate samples are analyzed at 1:25 based on action limits.

12.1.3.1 If there is more than one ZHE batch they may be combined, however, all ZHE blanks must be tested and proven to be free of contamination. If contamination is found in the ZHE blank, the other vial must be analyzed to confirm contamination. The affected samples must be footnoted appropriately. Only one is reported if both are proven free of contamination.

12.1.3.2 All leachate samples (including the Blank, LCS, MS/MSD, and sample duplicate (DUP) are diluted 1:25 based on action limits. The leachate is diluted by adding 2000 µL of the leachate extract to a 50 mL volumetric flask containing DI water. Dilute to a final volume of 1:25 using DI water. Fill a 40 mL unpreserved VOA vial with the prepared sample for analysis. If foaming is observed during dilution of the extract, 200 µL of anti-foaming agent (see 9.8) may be added to the 50mL volumetric flask to prevent foaming of the concentrator.

12.1.4 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample vial is sealed.

12.1.4.1 Dilutions may be made in volumetric flasks of various sizes. Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions. Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask. See Attachments V and VI.

12.1.4.2 Inject the proper aliquot of sample into the flask. Dilute the sample to the mark with organic-free reagent water. Cap the flask and invert three times. For samples requiring pH determination; once sample dilution is completed, the pH of the un-diluted sample must be taken with pH paper. If the pH is greater than 2 the sample must be footnoted to the nearest whole number. Repeat above procedure for additional dilutions.

12.1.4.3 Fill the vial with diluted sample and load onto the autosampler.

12.1.4.4 The autosampler adds the internal standard spiking solution and the surrogate spiking solution to the 5mL sample aliquot. The amount added by the autosampler should be equivalent to the concentration of 50 µg/L of each surrogate, 50 µg/L for the internal standards 1,4 dioxane d8 is at a concentration of 2000 µg/L and acetone d6 is at concentration of 100 µg/L). The archon accomplishes this by adding the internal standard and surrogate solution utilizing a 1 µL loop, the centurion w/s adds 5 µL of the solution. Analyze the samples using the same autosampler and GC conditions used to pass BFB, standard, and blank criteria.

12.1.5 If the initial analysis of sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences. Alternately, samples loaded on an autosampler can be accepted after a subsequent sample is shown to be free of carry-over contamination or if the detection is 10x greater than the carryover detection. Carryover in p&t systems can vary for instrument to instrument depending on the condition of the equipment. Analysts review the carryover after the upper level of the initial calibrations and after the ICV, in addition they monitor the carryover daily on the system blanks ran which is generally ran after QC samples.

12.1.5.1 It is routine for the laboratory to run multiple blanks after an initial calibration to monitor the carryover and ensure the ICV does not have carryover affecting the % recoveries. Daily, it is common for the laboratory to run system blank before the method blank. The system blank analyzed serves as a carry over assessment. It helps us determine how our system is performing from sample to sample and gives us a measure of how well our procedures for clean up are functioning on our instrumentation including rinses, baking, etc. As a secondary assessment, this allows us to determine if low level detections on our system are due to system contamination or from carryover which has become increasingly more important as we have a significant amount of clients that request evaluation and reporting to the statistical MDL levels. The second blank is used as the method blank but we feel that there is a benefit to us and the client in the analysis of 2 blanks for better assessment of system performance and data evaluation. All samples must be thoroughly reviewed when sample concentrations exceed 50µg/L to ensure low-level carryover is not occurring into subsequent analyses. Samples that need to be evaluated to the MDL are not re-analyzed if there are j-flagged detections in the method blank or the detections from possible sample carryover.

12.1.6 For matrix spike analysis, add 8.4 µL or 21 µL of a 100 µg /mL non-calibration source standard to the aqueous sample vial (42 mL actual volume). This is equivalent to a concentration of 20 µg/L or 50 µg/L, respectively, of each non-calibration source standard. Add the spiking solution through the septa of the vial as the vial should not be opened to maintain sample integrity.

12.1.7 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper calibration range for compounds which were previously over range.

12.1.8 Once sample analysis is completed, the pH of the sample must be taken using pH paper and recorded in the instrument run logbook. If the pH is greater than 2 and the holding time is past 7 days, the sample will be footnoted accordingly. The report number must be documented in the instrument run log and the sample data footnoted.

12.2 Sediment/Soil and Waste Samples

12.2.1 It is recommended that all samples of this type be screened prior to analysis. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-concentration method (0.004-0.2 mg/kg) or the mid-concentration method (>0.2 mg/kg). For both low level soils (LLS) and medium level soils (MLS) the pace label is placed on all containers during the log-in process which is performed by sample receiving. The weight of the label is subtracted from all soil samples to reflect the weight of the soil weight. The weight of the label is determined annually (unless specified) by weighing out 10 labels and determining an average weight. This subtracting of the label weight is performed in the soil prep logbook.

12.2.2 Low-Level Soils (LLS) - This is designed for samples containing individual purgeable compounds of <0.2 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and internal standards. Analyze all blanks and standards under the same conditions as the samples.

12.2.2.1 A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed by low level soil method. Follow the initial and daily calibration instructions, except the ICAL, CCVs, LCS/LCSD, Blanks are prepared by adding 5 mL of the solution into 40 mL unpreserved vial containing 5±0.1 g of sand and a stir bar purged at a temperature of 45-50ºC.

12.2.2.2 The majority of the samples received are sampled in Terracore kits (5035 closed system); therefore, the exact weight of the soil sample must be determined. Weigh the vial and record to the nearest 0.01 grams. Subtract the vial weight prior to sampling and record the final weight. The final weight is entered into Horizon to reflect to the soil weight. Refer to 7.2.3.4 for weight acceptance policy. The soil volume is critical to the purging of the sample. If there is too much soil in the vial, approximately more then ½" high in the vial, the autosampler purging needle can't purge the sample. The sample will be rejected for low level soil analysis and medium level analysis will occur instead. If there is soil in the threads of the capped vial, the sample will not seal properly and purging efficiency will be reduced which is generally indicated by monitoring the internal standards and can result in unreportable LLS analysis.

12.2.2.3 When a sample arrives and low level analysis is required (non- 5035), a 5 g aliquot of the sample is weighed directly into a tared unpreserved 40 mL vial. Note the weight to the nearest 0.01 g; add 5 mL of organic free DI water, and a stir bar.

12.2.2.4 The method blank is prepared by adding 5 mL of organic free DI water with 5+/-0.1g of sand and a stir bar. The LCS/LCSD is prepared by adding 5 mL of a mid-level calibration CCV solution to 5+/-0.1g of sand and a stir bar. The weight of the BLK, LCS, and LCSD are recorded as 5 grams so long as the actual weight is 5+/-0.1grams.

12.2.2.5 For matrix spike analysis, add 2.5 µL of the 100 µg/mL non-calibration source standard through the septa of the vial as the vial should not be opened to maintain sample integrity. This is the equivalent to a nominal concentration of 50 µg/kg for the majority of the analytes. Alternatively, if the MS/MSD is being prepared from a packed jar or encore, the MS/MSD may be prepared by adding 5 mL of a mid- level calibration CCV solution instead of spiking 2.5 µL of the 100 µg/mL non-calibration source standard through the septa of the vial. Which method is chosen it must be documented on the prep logbook.

12.2.2.6 Samples and QC are placed on a shaker table for 2 minutes to ensure samples are thoroughly mixed prior to purging.

12.2.2.7 The QC and samples are loaded onto the autosampler. The autosampler adds the internal standard spiking solution and the surrogate spiking solution to the soil sample with the addition of 10 mLs of DI water. The amount added by the autosampler should be equivalent to the concentration of 100µg/kg of each surrogate, 100µg/kg for the internal standards, and low level soils have 4,000 µg/kg for the 1,4-Dioxane d8 internal standard 200 µg/kg for acetone d6 (wet weight). The autosampler heats the sample at 45ºC throughout the purge cycle and stirs the magnetic stir bar.

12.2.2.8 If saturated peaks occurred the sample is either E-flagged or the medium level soil is prepared and analyzed for the analytes which exceeded the calibration range. If a non-closed system (5035) sample is provided, a smaller aliquot, 1 g or larger, may be used to dilute the analytes that exceeded the calibration range.

12.2.3 Medium Level Soil (MLS) - A sample is either extracted or diluted with methanol, depending on its solubility. An aliquot of the extract is added to organic-free reagent water. The autosampler adds the internal standard and surrogate spiking solution to the 5mL sample aliquot. The amount added by the autosampler should be equivalent to the concentration of 50 µg/L of each internal and surrogate standard. This is purged at ambient temperature. All samples with an expected concentration of > 1.0 mg/kg should be analyzed by this method.

NOTE: The following steps must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

12.2.4 To prepare the laboratory method blank (BLK), laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) weigh out 10+/-0.1 grams of Ottawa sand and add 10mL of methanol to a 40 mL VOA vial (42 mL actual volume). The weight of the BLK, LCS, LCSD are recorded as 10 grams so long as the actual weight is 10+/-0.1grams. They should be uniquely labeled by QC batch numbers to ensure they are analyzed with the correct batch of samples. The LCS/LCSD are spiked with the 100 µL of 100ug/mL of the non-calibration source standard to achieve a final concentration of 1000 µg/kg after the 1:50 dilution.

12.2.5 To prepare the matrix spike (MS) and matrix spike duplicate (MSD), weigh the vial and record the weight to the nearest 0.01g. Subtract the vial weight prior to sampling and record the final weight. If the weight is greater than the expected 5g, 10g, or 25g weight, the addition of methanol is necessary in order to maintain the 1:1 sample to solvent ratio. Add the appropriate amount of the 100 µg/mL of the non-calibration source standard to achieve a final concentration of 1000 µg/kg after the 1:50 dilution. If insufficient sample volume was received to prepare the MS/MSD, the project must be footnoted.

12.2.6 To prepare samples that arrive preserved in methanol, weigh the vial and record to the nearest 0.01g. Subtract the vial weight prior to sampling and record the final weight. If

the weight is greater than the expected 5g, 10g, or 25g weight, the addition of methanol is necessary in order to maintain the 1:1 sample to solvent ratio. If the weight is less than expected 5g, 10g or 25g weight, record the difference.

12.2.7 To prepare samples that are not preserved in methanol, the sample consists of entire contents of sample container. Using a top-loading balance, weigh 10 grams (wet weight) of the sample into a tared 40 mL vial. Record the weight to 0.01g. Samples not field preserved should be preserved within 48 hours of collection. Client, QAPP, or state requirements may supersede this requirement.

12.2.8 Oily, solid waste or product samples are generally not field preserved due to the unknown solubility. If the sample is not soluble in water, a waste dilution will be performed by weighing out 1gram of the sample into a tared 40 mL VOA vial. Record the weight to 0.01g. Dilute with the addition of 10 mL of P&T grade methanol. Note the prep method as a waste dilution on the prep log.

12.2.9 The pace label that is applied in sample receiving is subtracted from the soil weight to eliminate the label weight from biasing the soil weight. The label weight was determined to be 0.18 grams by averaging 10 labels and all samples have this subtraction done in our prep sheets. If additional labels are applied the lab is unable to determine the weight of those labels and therefore unable to determine the potential bias in the weight/reporting limits.

12.2.10 The LCS/LCSD, MS/MSD, BLK, and all associated samples within the batch must be shaken for two minutes, and then sonicated for 20 minutes. After sonicating, prepare the samples by adding 1000 µL either by syringe or eppendorf pipetter of the methanol extract to a 50 mL volumetric flask containing DI water. Dilute to a final volume of 1:50 using DI water. Fill a 40 mL VOA vial with the prepared sample for analysis.

12.2.11 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample vial is sealed.

12.2.11.1 Dilutions may be made in volumetric flasks of various sizes. Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

12.2.11.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask. See attachment III for common dilution factors.

12.2.11.3 Inject the proper aliquot of sample extract into the flask and the proper amount of P&T methanol, so that the same amount of methanol is added to all samples and QC. Dilute the sample to the mark with organic-free reagent water. Cap the flask and invert three times.

12.2.12 The extracts must be stored above freezing but <6°C.

12.3 Data Interpretation

12.3.1 Qualitative Analysis: An analyte is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component, and (2) correspondence of the sample component and the standard component mass spectrum.

12.3.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample. If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

12.3.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum. (2) The relative intensities of ions specified in (1) must agree within ± 30% between the standard and sample spectra. Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20 and 80 percent.

12.3.2 For samples containing components not associated with the calibration standards, a library search using the most recent NIST/EPA Library may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

12.3.2.1 Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

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

12.3.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.3.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

12.3.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

12.3.2.6 Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

13. Quality Control

13.1. Table 13.1 Quality Control.

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per batch of 20 samples or less	Target analytes must be less than 1/2 reporting limit. If results are reported to MDL, target analytes in MB should be non-detect to ½ PRL. The lab is not able to routinely achieve MB less than the MDLs due to common p&t	Re-analyze associated samples. ***Exceptions:*** If sample ND, report sample without qualification; If sample result >10x MB detects, report sample as not impacted by the blank contamination; If sample result <10x MB detects and the sample cannot be reanalyzed, report sample with appropriate qualifier. Client must be alerted and

			carryover and common lab contamination.	authorize this condition. If there is insufficient sample volume B flag the detections present in the samples associated with the contaminated blank. For WI samples, evaluate the MB to the MDL. If detections are present between the MDL and RL, qualify appropriately. For detections above the RL, data is acceptable to report only if sample concentrations are 10x greater, otherwise re-prep and re-analyze.
Laboratory Control Sample (LCS)	DI water spiked with all target compounds for waters and Low level soils. Medium level soils are extracted in 10mLs of methanol. LCS/LCSDs prepared using non-calibration source standard	One per batch of 20 samples. A LCSD is not required per method requirement and generally only performed if insufficient volume for MS/MSD or MS/DUP.	Internally generated limits updated annually. For LCSs containing a large number of analytes, it is statistically likely that a few recoveries will be outside of the control limits. This does not necessarily mean the system is out of control, and therefore no corrective action would be required beyond footnoting the data. Client, QAPP, or state requirements may supersede this requirement. See Quality Manual section 4.2 for more information.	The number of allowable exceedance is as follows: ->90 analytes in LCS- 5 outliers -71-90 analytes in LCS- 4 outliers -51-70 analytes in LCS- 3 analytes -31-50 analytes in LCS- 2 outliers 11-30 analytes in LCS- 1 outlier -<11 analytes in LCS- no outliers allowed Evaluate the LCS to determine the cause of the outliers; verify calculations and standard preparation. Perform any necessary system maintenance prior to reanalyzing the LCS. For waters, this is the same as the CCV solution so the associated samples will have to be reanalyzed accordingly. ***Exceptions:*** If LCS recovery is > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Client sample spiked with all target compounds Prepared using non-calibration source standard	One per batch of 20 samples or less	Internally generated limits updated annually	If LCS and MBs are acceptable, the MS/MSD chromatogram should be reviewed and it may be reported with appropriate footnote indicating matrix interferences. Determine that there was no system error causing the outlier, reanalyze if necessary per client or regulatory QAPP.
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup Prepared using non-calibration source	One per batch of 20 samples or less MS/MSD is the method requirement if	%Diff ≤ 30%	Report results with an appropriate footnote. For Minnesota Admin Contract clients – all MS/MSD failures require reanalysis of the MS/MSD and the

	standard	sufficient sample volume is available. If insufficient vials are available perform a MS of one sample and a Dup of another in the batch. For MPCA/Admin Contract clients, if there is insufficient volume for the MS/MSD, perform and MS/LCSD		original sample. If it is still out of control, investigate and document the cause in the associated narrative as well as qualifying appropriately. For Minnesota Admin Contract clients, if there is insufficient volume for MS/MSD, qualify the batch for the insufficient volume even if a MS/DUP is performed as the MS/MSD are required.
Surrogate	1,2 Dichloroethane d4 Toluene d8 4-Bromofluorobenzene (BFB)	In every analytical run. Surrogates are spiked into the sample utilizing the autosampler using a single point calibration for waters, low level soils and medium level soils.	Internally generated limits updated annually	Check to make sure there are no calculation errors, surrogate solutions or internal standard errors. Recalculate accordingly if found. Check instrument performance, if it is correct and reanalyze accordingly. Reanalyze to confirm outlier. If confirmed, report the initial analysis and indicate confirmed by second analysis. If it doesn't confirm, report the second analysis if within holding time. If the methanol preserved soil is methanol corrected see section 14.9 for outliers details. ***Exception:*** if the surrogates are out biased high and the sample is non-detect, report the data with the surrogates qualified accordingly or if visual matrix affecting the surrogate recovery data may be reported with footnotes.

14. Data Analysis and Calculations

14.1. The following calculation can be used to calculate the LCS or MS percent recovery (where SampleConc would be equal to 0 for the LCS and MSConc would be the LCS concentration):

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue} * 100$$

Where:
MSConc = MS Concentration
SampleConc = Sample Concentration of the MS parent sample

14.2. %REC = % Recovery The RF is calculated as follows:

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

Where:
A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard (µg/L).
C_x = Concentration of the compound being measured (µg/L).

14.3. The percent relative standard deviation (%RSD) for CCCs:

$$\%RSD = \frac{SD}{\overline{X}} x100$$

Where: **RSD** = Relative standard deviation.
SD = Standard deviation of average RFs for a compound
$\overline{X}$ = Mean of initial RFs for a compound

14.4. Standard deviation is calculated as below:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_1 - \overline{RF}\right)^2}{n-1}}$$

Where: $\mathbf{RF_1}$ = Each individual response factor
$\overline{\mathrm{RF}}$ = Mean of the Response Factor
n = The total number of values

14.5. Percent Difference (%D) for daily CCV evaluation:

$$\%Difference = \frac{RF_1 - RF_c}{RF_1} x100$$

Where: $\mathbf{RF_1}$ = Average response factor from initial calibration.
$\mathbf{RF_c}$ = Response factor from current verification check standard

14.6. Quantitative Analysis: When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used should be the one nearest the retention time of that of a given analyte or as specified in the method.

Calculate the concentration of each identified analyte in the sample as follows:

Water and Water-Miscible Waste:

$$\text{Concentration}(\mu g/L) = \frac{(A_x)(I_s)(DF)}{(A_{is})(RRF)}$$

Where:

$\mathbf{A_x}$ = Area of characteristic ion for compound being measured.

$\mathbf{I_s}$ = Amount of internal standard injected (µg/L).

$\mathbf{A_{is}}$ = Area of characteristic ion for the internal standard.

RRF = Average Relative Response factor for compound being measured.

DF = Dilution Factor

Sediment/Soil, Sludge, and Waste:

$$High\ \text{Conc.}\ (\mu g/\text{kg}) = \left[\frac{(A_x)(I_s)(DF)(V_t)}{(A_{is})(RRF)(W_s)}\right] \bullet 50$$

$$Low\ \text{Conc.}\ (\mu g/\text{kg}) = \frac{(A_x)(I_s)}{(A_{is})(RRF)(W_s)}$$

Where:

A_x, I_s, A_{is}, RRF = Same as in water and water-miscible waste above
V_t = Volume of total extract (mL)
V_i = Volume of extract added (mL) for purging
W_s = Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.
S_v = Volume of diluted extract
DF = Dilution factor

Note: All methanol extracts are diluted 1:50

14.7. Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The percent dry weight of the sample should be reported along with the data in either instance.

14.8. When applicable, an estimate of concentration for non-calibrated components in the sample can be made. The formula given above should be used with the following modifications: The areas Ax and Ais should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentrations. Use the nearest internal standard free of interferences.

14.9. Methanol Correction: This will only be performed if specifically requested by a regulatory agency or by the client. When methanol correction is requested, the volume needs to be adjusted for the amount of soil moisture present in the solid sample. This is done through Horizon once the % moisture analysis has been performed. The analyst enters the sample weight and volume into the prep batch in Horizon. The condition code needs to be changed to "mc" for methanol corrected instead of the standard "ok". Once this is done, Horizon will perform the calculation. The final volume will change in Horizon to reflect the methanol correction. Note: the lab will spike the surrogate solution (if applicable) based on the known actual volume methanol in the sample, not the methanol corrected volume. Depending on the % moisture in the sample(s) the lab has seen circumstances where the methanol corrected volume is artificially higher than it visually appears. It is not uncommon to have the surrogate recoveries fail once moisture is corrected. The lab will not re-run for surrogate confirmation if non-methanol corrected surrogate recoveries are within control limits.

14.10. Methanol Correction Formula:

14.11. Methanol Corrected Volume = Volume of methanol(mL) + ((%_percent_moisture * sample weight(g))/100))

14.12. The methanol corrected volume value obtained becomes Vt in the calculation referenced in section 14.6.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See tables in section 11 & 13.

16. Corrective Actions for Out-of-Control Data

16.1. See tables in section 11 & 13.

16.2. SPCC Criteria Failed: If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. SPCCs are used to check compound instability and to check degradation caused by contaminated lines or active sites in the system. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. Chloromethane is most likely compound to be lost if the purge flow is too fast. Bromoform is one of the compounds most likely to be purged very poorly in the purge flow is too slow. Cold spots and/or active sites in the transfer line may adversely affect response. Response of quantiation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z may improve bromoform response. 1,1,2,2 Tetrachloroethane and 1,1 dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

16.3. CCC Failure: If the percent difference for any non-CCC analyte is greater than 40%, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (>20% difference), for any one CCC, corrective action should be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration should be generated. This criterion should be met before quantitative sample analysis begins.

16.4. CCV Failure: If the first CCV fails, the analyst should try to determine the root cause for the failure. Some possible reasons for failures may include but not limited to: bad CCV solution, bad spike of CCV standard, standard mix degradation, internal standard fluctuation/change, analytical system not conditioned, active sites and/or cold sites in the trap or concentrator, contaminated system due to dirty samples, or analytical conditions changed over time. Corrective action for a failed CCV will be case by case depending on the root cause. The analyst's expertise in determining the root cause will help determine the corrective action. Some common corrective actions may include not limited to: making a new CCV solution, running a different vial of a CCV solution, using a different standard to make the CCV solution, making new standards and new CCVs, baking out the concentrator, or replacing transfer lines on concentrator. For volatiles there is generally no major maintenance performed on a daily basis to maintain calibration. If major maintenance is required the system then needs to be recalibrated. If the 2nd ccv fails to meet criteria, a new initial calibration curve must be performed.

16.5. Internal Standard Failures: Internal standard recoveries out low (high bias) – if compounds associated with the internal standard(s) that are outside the control limits are non-detect, the sample can be reported without re-analysis, however, if the outlier is not indicative of a system drift (i.e. If only one sample has internal standard drift, which is dissimilar from other samples around the injection time), re-analysis should be performed to rule out matrix effects. Internal standard recoveries out high (low bias) – re-analysis should be performed assuming there is sufficient sample volume remaining. Appropriate footnoting practices are also observed.

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

17.1. If not specifically listed in the tables in section 11 & 13, the contingencies are as follows. If there is no additional sample volume to perform re-analyses, all data will be reported as final with applicable qualifiers. If necessary, an official case narrative will be prepared by the Quality Manager or Project Manager.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually (per the method) per S-MN-Q-269, Method Detection Limit Studies for each matrix per instrument.

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-MN-Q-279, Training and Employee Orientation.

18.4. **Periodic proficiency testing (PT)** samples are analyzed to demonstrate continuing competence per SOP S-MN-Q-258, or equivalent replacement. Results are filed in the Quality office.

19. Method Modifications

19.1. 8260B is a performance based method from SW-846. Some modifications include the use of Nitrogen as purge gas, faster GC ramp parameters reduced purge times, increased purge flow rates, reduced bake times, reduced desorb times, and some systems use a heated purge at 40ºC for water,

Below are the typical GC parameters and Concentrator parameters

Typical GC/Concentator paramaters	
Start Temp (^{o}C):	45
Initial Time (min):	2.75
Initial Rate (^{o}C/min):	30/min to 155, hold for 0.5 min
Final Temp (^{o}C):	32/min to 220 hold for 0.5min
Final Time (min):	0.29
Total GC Run Time(min)	~9.5 min
Inlet Temp (^{o}C):	250
Detector Temp (^{o}C):	180
Purge Temp (^{o}C):	ambient-50*
Purge Time (min):	5.0-11.0
Purge Flow (mL/min):	~40-60
Desorb Time (min):	0.5-2.0
Desorb Temp (^{o}C):	250-260
Bake Time (min):	2.0-7.0
Bake Temp (^{o}C):	270
Column Type:	Restek RTX-VMS
Column Dimensions:	20m/0.18mmID/1um df
Column Flow (mL/min):	0.8
Split Flow	30:1 to 60:1
* EVOs that run waters purge temp 30-40C; tekmar 3000/3100/atomx are ambient; MLS are ambient; LLS are 50C via soil cup of autosampler.	

These parameters are for the typical GC/MS system. Some systems may differ depending on the analyte list/matrix/RL needed for the analysis that runs on each different instrument.

19.2. The tuning criteria follow the guidelines indicated in Appendix C: CLP/SOW OLC02.1/Low Concentration Volatile Organic Analysis Method QC criteria, Equations and Definitions.

19.3. The primary ion used for 2-Butanone and 4-Methyl-2-Pentanone are based on the Appendix A: CLP/SOW OLM03.2/Volatile Organic Analysis. In addition, the ion selected for 2-Butanone is due to the fact that 2-Butanone coelutes with 1,1-Dichloropropene. Ion 43 is being utilized as that is not a common ion with the co-eluting compound.

19.4. The lab compares the internal standard to the daily mid-point standard level (CCV) and the CCV is compared to the initial calibration for retention time. This is a modification of the method as written due to client data quality objectives.

19.5. Pace utilizes a single point calibration for surrogates as noted in section 13. This is a deviation of Method 8000B and 8000C based on the guidance in EPA 8260C section 11.3.3. It is demonstrated through acceptable initial calibration, ICV, CCV, sample and batch QC performance.

19.6. The CCV is prepared using non-calibration source standard to allow for LCS/CCV interchangeability, the ICV is also commonly used as CCV/LCS when sample analysis follows calibration.

20. Instrument/Equipment Maintenance

20.1 Please refer to the GC/MS 6890 instrument manual for maintenance procedures performed by the lab.

20.2 All maintenance activities are listed daily in maintenance logs that are assigned to each separate instrument.

21. Troubleshooting

21.1. The purge and trap concentrator must be leak free in order to ensure properly sample purge efficiency and desorbation. If analyst notices significant decrease in response and suspects a possible leak, one can leak check the concentrator to ensure the p&t concentrator is free for leaks. This can be done through the software or manually by capping the vent valve of the concentrator and purging a blank.

22. Safety

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

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

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-MN-S-003, Waste Handling.

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

24. Pollution Prevention

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

25. References

25.1. Pace Quality Assurance Manual- most current version.

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

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

25.4. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Method 8260B.

25.5. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Method 5035.

25.6. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Method 5030B.

25.7. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Update III, Method 8000B.

25.8. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Online, Method 8260C.

25.9. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Online, Method 5035A.

25.10. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Online, Method 5030C.

25.11. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Online, Method 8000C.

25.12. Appendix C: CLP/SOW OLC02.1/Low Concentration Volatile Organic Analysis Method QC criteria, Equations and Definitions.

25.13. Appendix A: CLP/SOW OLM03.2/Volatile Organic Analysis

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Attachment I: Method 8260B Analyte List, PRL, Characteristic Mass (m/z), and associated IS for Restek VMS- Rtx Column.

26.2. Attachment II: Characteristic Ions for TCLP Target Compounds.

26.3. Attachment III: Analytes and Limits for TCLP Compounds

26.4. Attachment IV: Standard 8260 Volatiles Target List

26.5. Attachment V: Common Dilution Factors for Water Samples

26.6. Attachment VI: Common Dilution Factors for TCLP Samples

26.7. Attachment VII: Common Dilution Factors for Medium Level Soil Samples

26.8. Attachment VIII: 1,4 Dioxane by SIM Modified Method 8260B

27. Revisions

Revision Number	Reason for Change	Date
S-MN-O-521-Rev.35	Added Sections 11.7 and 11.8 and all subsections.	11Jul2018

Attachment I: Method 8260B Analyte List, PRL, Characteristic Mass (m/z), and associated IS for Restek VMS- Rtx Column

Analyte	CAS Number	Low Level Waters (µg/L)	Waters (µg/L)	Low-Level Soils (µg/kg)**	Medium Level Soils (µg/kg)***	Primary Ion	Secondary Ion(s)	Internal Standard used for Quantitation
Propylene	115-07-01	1	1	4	50	41	39,42	1
Dichlorodifluoromethane	75-71-8	1	1	10	50	85	87	1
Chloromethane	74-87-3	4	4	10	200	50	52	1
Vinyl Chloride	75-01-4	0.2	0.4	4	20	62	64	1
1,3- Butadiene	106-99-0	1	1	4	50	54	39	1
Bromomethane	74-83-9	4	4	20	500	94	96	1
Chloroethane	75-00-3	1	1	10	500	64	66	1
Trichlorofluoromethane	75-69-4	0.5	1	10	200	101	103	1
Dichlorofluoromethane	75-43-4	1	1	4	500	67	69	1
Diethyl Ether	60-29-7	4	4	10	200	59	45, 74	1
Ethanol	64-17-5	80	80	400	NA	45	46	4
1,1-Dichloroethene	75-35-4	0.5	1	4	50	96	61, 63	1
Carbon Disulfide*	75-15-0	1	1	4	50	76	78	1
Trichlorotrifluoroethane	76-13-1	1	1	4	50	101	151, 103	1
Iodomethane	74-88-4	4	4	10	200	142	127,141	1
Acrolein	107-2-8	10	10	100	2000	56	55	1
Allyl Chloride	107-05-1	4	4	10	200	41	76,39	1
Acetone d6 (IS#2)	666-52-4	IS	IS	IS	IS	46	64	
Isopropanol (2-Propanol)	67-63-0	100	100	NA	NA	45	43	4
Methylene Chloride*	75-09-2	4	4	20	200	84	86	1
Acetone*	67-64-1	20	20	20	1000	58	43	2
trans-1,2-Dichloroethene	156-60-5	0.5	1	4	50	96	61,98	1
Methyl Acetate	79-20-9	5	5	Na	Na	74	43	
Hexane (n-Hexane)*	110-54-3	10	10	500	500	86	57,56	2
Methyl-tert-butyl Ether	1634-04-4	0.5	1	4	50	87	57	1
Tert Butyl Alcohol (2-Methyl-2-propanol) (TBA)	75-65-0	10	40	100	5000	59	41	4
Acetonitrile*	75-05-8	100	100	NA	NA	41	40,39	1
Isopropyl Ether (Diisopropyl ether)	108-20-3	1	1	4	200	45	87,59	1
Chloroprene	126-99-8	1	1	NA	NA	53	88,90	1
1,1-Dichloroethane	75-34-3	0.5	1	4	50	63	65, 83	1
Acrylonitrile	107-13-1	10	10	100	2000	53	52,51	1
ethyl tert-butyl ether	637-92-3	0.5	1	4	200	59	87	1
Vinyl Acetate	108-05-4	10	10	10	500	43	86	1
cis-1,2-Dichloroethene	156-59-2	0.5	1	4	50	96	61,98	1

Analyte	CAS Number	Low Level Waters (µg/L)	Waters (µg/L)	Low-Level Soils (µg/kg)**	Medium Level Soils (µg/kg)***	Primary Ion	Secondary Ion(s)	Internal Standard used for Quantitation
2,2-Dichloropropane	594-20-7	1	4	10	200	77	97	1
Cyclohexane*	110-82-7	5	5	10	250	56	84,41	1
Bromochloromethane	74-97-5	1	1	4	50	130	49, 128	1
Chloroform	67-66-3	0.5	1	4	50	83	85	1
Carbon Tetrachloride	56-23-5	1	1	4	50	117	119	1
Tetrahydrofuran	109-99-9	10	10	40	2000	72	71,42	2
Ethyl acetate	141-78-6	5	5	NA	NA	43	61,70	1
1,1,1-Trichloroethane	71-55-6	0.5	1	4	50	97	99,61	1
Dibromofluoromethane (S)	1868-53-7	SS	SS	SS	SS	113		1
Sec-Butyl alcohol	78-92-2	40	40	NA	NA	45	59	4
1,1-Dichloropropene	563-58-6	0.5	1	4	50	75	110,77	1
2-Butanone (MEK)*	78-93-3	5	5	20	250	43	72	1
2,2,4-trimethylpentane *	540-84-1	4	4	-	-	57	56	1
Benzene	71-43-2	0.5	1	4	20	78	77	1
Propionitrile	107-12-0	40	40	NA	NA	54	55,52	1
Methacrylonitrile	126-98-7	4	5	NA	NA	41	67,39	1
Pentafluorobenzene (IS#1)	363-72-4	IS	IS	IS	IS	168		
tert-amyl methyl ether	994-05-8	0.5	1	4	200	73	87,55	1
1,2 Dichloroethane d4 (S)	17060-07-0	SS	SS	SS	SS	65	67,51	1
1,2-Dichloroethane	107-06-2	0.5	1	4	50	62	98	1
Isobutanol	78-83-1	80	80	400	4000	43	41,42	4
tert-amyl alcohol	75-85-4	10	10	100	5000	59	73,55	4
methylcylohexane	108-72-2	1	1	Na	Na	98	83,55	1
Trichloroethene	79-01-6	0.4	0.4	4	50	130	95, 132	3
1,4 Difluorobenzene (IS #3)	540-36-3	IS	IS	IS	IS	114		
Tert-amyl ethyl ether	919-94-8	0.5	1	4	200	59	87, 73	3
Dibromomethane	74-95-3	0.5	4	4	50	174	95,93	3
n-Butanol	71-36-3	200	200	NA	NA	56	41,43	4
1,2-Dichloropropane	78-87-5	4	4	4	50	63	112	3
Bromodichloromethane	75-27-4	0.5	1	4	50	83	85,127	3
Ethyl Acrylate	140-88-5	4	5	NA	NA	55	56	3
1,4 Dioxane-d8 (IS #4)	17647-74-4	IS	IS	IS	IS	96	64	
1,4-Dioxane	123-91-1	200	200	400	10000	88	58,57	4
Methyl Methacrylate	80-62-6	4	5	NA	NA	69	41,100	3
3-Pentanone	96-22-0	4	4	NA	NA	57	86	3
2-Chloroethyl Vinyl Ether	110-75-8	10	10	25	500	63	106, 65	3
cis-1,3-Dichloropropene	10061-01-5	0.5	4	4	50	75	77, 39	3

Analyte	CAS Number	Low Level Waters (µg/L)	Waters (µg/L)	Low-Level Soils (µg/kg)**	Medium Level Soils (µg/kg)***	Primary Ion	Secondary Ion(s)	Internal Standard used for Quantitation
Toluene d8 (S)	2037-26-5	SS	SS	SS	SS	98	100	5
Toluene	108-88-3	0.5	1	4	50	92	91	5
2-Nitropropane	79-46-9	10	10	NA	NA	43	41, 39	5
Tetrachloroethene	127-18-4	0.5	1	4	50	166	168, 129	5
4-Methyl-2-Pentanone (MIBK)*	108-10-1	5	5	20	250	43	58, 85	5
trans-1,3-Dichloropropene	10061-02-6	0.5	4	4	50	75	77,39	5
1,1,2-Trichloroethane	79-00-5	0.5	1	4	50	97	83, 85	5
4-Methyl-2-pentanol	108-11-2	40	40	NA	NA	45	69,87	4
Ethyl Methacrylate	97-63-2	4	5	NA	NA	69	41,99	5
Dibromochloromethane	124-48-1	0.5	1	4	50	129	127	5
1,3-Dichloropropane	142-28-9	0.5	1	4	50	76	78	5
1,2-Dibromoethane	106-93-4	0.5	1	4	50	107	109, 188	5
2-Hexanone*	591-78-6	5	5	20	250	43	58, 57	5
Chlorobenzene d5 (IS#5)	3114-55-4	IS	IS	IS	IS	117		
Chlorobenzene	108-90-7	0.5	1	4	50	112	77, 114	5
Ethylbenzene	100-41-4	0.5	1	4	50	91	106	5
1,1,1,2-Tetrachloroethane	630-20-6	0.5	1	4	50	131	133, 119	5
m&p-Xylene	7816-60-0	1	2	8	100	106	91	5
o-Xylene	95-47-6	0.5	1	4	50	106	91	5
Bromoform	75-25-2	4	4	20	200	173	175,254	5
Styrene	100-42-5	0.5	1	4	50	104	78	5
Isopropyl benzene (Cumene)	98-82-8	0.5	1	4	50	105	120	5
4-Bromofluorobenzene (BFB) (S)	460-00-4	SS	SS	SS	SS	95		6
Bromobenzene	108-86-1	0.5	1	4	50	156	77,158	6
Cis-1,4-Dichloro-2-butene	1476-11-5	4	4	NA	NA	53	77, 75	6
n-Propylbenzene	103-65-1	0.5	1	4	50	91	120	6
1,1,2,2-Tetrachloroethane	79-34-5	0.5	1	4	50	83	131, 85	6
2-Chlorotoluene	95-49-8	0.5	1	4	50	91	126	6
1,2,3-Trichloropropane	96-18-4	4	4	4	200	110	75, 112	6
4-Ethyltoluene	622-96-8	1	1	4	50	105	120	6
1,3,5-Trimethylbenzene	108-67-8	0.5	1	4	50	105	120	6
Trans-1,4-Dichloro-2-butene	110-57-6	10	10	50	500	53	88, 75	6
4-Chlorotoluene	106-43-4	0.5	1	4	50	91	126	6
tert-Butylbenzene	98-06-6	0.5	1	4	50	119	91,134	6
1,2,4-Trimethylbenzene	95-63-6	0.5	1	4	50	105	120	6
sec-Butylbenzene	135-98-8	0.5	1	4	50	105	134	6

Analyte	CAS Number	Low Level Waters (µg/L)	Waters (µg/L)	Low-Level Soils (µg/kg)**	Medium Level Soils (µg/kg)***	Primary Ion	Secondary Ion(s)	Internal Standard used for Quantitation
Dicyclopentadiene	77-73-6	4	4	4	200	66	39,132	6
p-Isopropyltoluene	99-87-6	0.5	1	4	50	119	134, 91	6
1,3-Dichlorobenzene	541-73-1	0.5	1	4	50	146	111, 148	6
1,4-Dichlorobenzene-d4 (IS#6)	3855-82-0	IS	IS	IS	IS	152		
1,4-Dichlorobenzene	106-46-7	0.5	1	4	50	146	111, 148	6
1,2,3-Trimethylbenzene	526-73-8	1	1	NA	NA	105	120	6
n-Butylbenzene	104-51-8	0.5	1	4	50	91	92, 134	6
1,2-Dichlorobenzene	95-50-1	0.5	1	4	50	146	111, 148	6
1,2-Dibromo-3-chloropropane	96-12-8	4	4	10	500	75	155,157	6
Hexachloro-1,3-butadiene	87-68-3	1	1	10	250	225	227,223	6
1,2,4-Trichlorobenzene	120-82-1	0.5	1	4	50	180	182, 145	6
Naphthalene	91-20-3	1	4	10	200	128		6
1,2,3-Trichlorobenzene	87-61-6	0.5	1	4	50	180	182, 145	6
2-Methylnaphthalene*	91-57-6	5	5	20	250	142	141	6
Xylene (total)	1330-20-7	1.5	3	12	150	NA	NA	5
1,2-Dichloroethene (total)	540-59-0	1	2	8	100	NA	NA	1
BTEX (total)	N/A	1	2	NA	NA	NA	NA	1,5
Total 1,3-Dichloropropene	NA	1	8	NA	NA	NA	NA	3,5

*Can be lab contaminate and therefore MDL set to ½ PRL and not statistical MDL.**Reporting limit for a 5g soil preserved with 5mL DI water ***Reporting limit for a 25g/10g soil preserved with 25mL/10mL methanol

1,4 Dioxane-d8 internal standard is used to quantify the water soluble compounds. Acetone d6 is used to quantify acetone, THF and hexane.

Note: Hexane uses 86 as the primary ion due to co-elution with MTBE.

Important NOTE: Reporting Limits may vary. For the most current reporting limits, refer to HORIZON.

Attachment II: Characteristic Ions for TCLP Target Compounds

Parameter	Primary Ion	Secondary Ions
Vinyl chloride	62	64
1,1-Dichloroethene	96	61, 63
Chloroform	83	85
1,2–Dichloroethane	62	98
2-Butanone	43	72
Carbon tetrachloride	117	119, 121
Trichloroethene	130	95, 132
Benzene	78	77
Tetrachloroethene	166	168, 129
Chlorobenzene	112	77, 114
1,4- Dichlorobenzene	146	111, 148

Attachment III: Analytes, Quantitation Limits and Regulatory Levels for TCLP Compounds

Parameter	CAS Number	Quantitation Limit (µg/L)	Regulatory Level (µg/L)
Vinyl chloride	75-01-4	10	200
1,1-Dichloroethene	75-35-4	25	700
Chloroform	67-66-3	25	6,000
1,2-Dichloroethane	107-06-2	25	500
2-Butanone	78-93-3	100	200,000
Carbon tetrachloride	56-23-5	25	500
Trichloroethene	79-01-6	25	500
Benzene	71-43-2	25	500
Tetrachloroethene	127-18-4	25	700
Chlorobenzene	108-90-7	25	100,000
1,4- Dichlorobenzene	106-46-7	25	7,500

Attachment IV: Standard 8260B Volatile Target List

ANALYTE NAME	ANALYTE NAME
1,1-Dichloroethane	1,1-Dichloroethene
1,1-Dichloropropene	1,1,1-Trichloroethane
1,1,1,2-Tetrachloroethane	1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane	1,1,2-Trichlorotrifluoroethane
1,2-Dichlorobenzene	1,2-Dichloroethane
1,2-Dichloropropane	1,2,3-Trichlorobenzene
1,2,3-Trichloropropane	1,2,4-Trichlorobenzene
1,2,4-Trimethylbenzene	1,3-Dichlorobenzene
1,3-Dichloropropane	1,3,5-Trimethylbenzene
1,4-Dichlorobenzene	2,2-Dichloropropane
2-Chlorotoluene	4-Chlorotoluene
Acetone	Allyl chloride
Bromochloromethane	Benzene
Bromobenzene	Bromoform
Bromomethane	Cis-1,2-Dichloroethene
Cis-1,3-Dichloropropene	Carbon Tetrachloride
Chlorodibromomethane	Chlorobenzene
Chloroethane	Chloroform
Chloromethane	1,2-Dibromo-3-chloropropane
Dibromomethane	Dichlorodifluoromethane
Dichlorofluoromethane	1,2-Dibromoethane
Ethylbenzene	Ethyl ether
Hexachlorobutadiene	Isopropylbenzene
Methylene chloride	Methyl ethyl ketone
Methyl isobutyl ketone	Methyl tertiary butyl ether
n-Butylbenzene	Naphthalene
n-Propylbenzene	o-Xylene
p&m-Xylene	p-Isopropyltoluene
Sec-Butylbenzene	Styrene
Tert-Butylbenzene	Trans-1,2-Dichloroethene
Trans-1,3-Dichloropropene	Trichloroethene
Trichlorofluoromethane	Tetrachloroethene
Tetrahydrofuran	Toluene
Vinyl chloride	Bromodichloromethane

Attachment V: Common Dilution Factors for Water Samples

Water Dilution Factors		
Dilution	**Into 50 mL**	**Into 100 mL**
2x	25 mL	n/a
5x	10 mL	20 mL
10x	5 mL	10 mL
20x	2.5 mL	5 mL
25x	2 mL	4 mL
50x	1000 uL	2 mL
100x	500 uL	1000 uL
200x	250 uL	500 uL
500x	100 uL	200 uL
1000x	50 uL	100 uL
10000x	5 uL	10 uL

Attachment VI: Common Dilution Factors for TCLP Samples

Pace Analytical®	Document Name: **TCLP Dilution Factors**	Document Revised: 28Feb2018 Page 1 of 1
	Document No.: **F-MN-O-138-rev.04**	Issuing Authority: Pace Minnesota Quality Office

TCLP Dilution Factors		
Dilution	**Into 50 mL**	**Into 100 mL**
1x	2 mL	4 mL
2x	1 mL	2 mL
5x	400 µL	800 µL
10x	200 µL	400 µL
20x	100 µL	200 µL
50x	40 µL	80 µL
100x	20 µL	40 µL

Attachment VII: Common Dilution Factors for Medium Level Samples

Soil Dilutions into 50mLVolumetric		
Dilution Factor	Volume of Soil Extract (uL)	Volume of P&T Methanol (uL)
1	1000	0
2	500	500
5	200	800
10	100	900
20	50	950
25	40	960
50	20	980
100	10	990
200	5	995
500	2	998
1000	1	999
Beyond 1000x Serial Dilutions are performed.		

Soil Dilutions into 100mLVolumetric		
Dilution Factor	Volume of Soil Extract (uL)	Volume of P&T Methanol (uL)
1	2000	0
2	1000	1000
5	400	1600
10	200	1800
20	100	1900
25	80	1920
50	40	1960
100	20	1980
200	10	1990
500	4	1996
1000	2	1998
Beyond 1000x Serial Dilutions are performed.		

Form O139Rev.01 30Jan2008

ATTACHMENT VIII: 1,4 Dioxane by 8260B SIM

Analyte	CAS Number	Reporting Limit in ug/L	Primary Ion	Secondary Ion	Internal Standard	Surrogate
1,4 Dioxane by SIM	123-91-1	1	88	58	1,4 dioxane d8	Toluene-d8

Standard	Standard(s) Amount	Solvent	Solvent Diluent Volume	Final Total Volume	Final Concentration
Intermediate Tune Solution	500 µL	MeOH	100 mL	50 µg/mL	Intermediate Tune Solution
Tune	5 µL	Water	5 mL	50 µg/L	Tune
Calibration Working Standard	0.5 mL of 1000 – 40,000 mg/L	MeOH	9.5 mL of MeOH	10.0 mL	50 - 2000 µg/mL (nominal conc. 100 µg/mL)
Calibration Std 1	0.5 µL		99.999 H_2O	100 mL	0.5 µg/L
Calibration Std 2	1.0 µL		99.997 H_2O	20 mL	1.0 µg/L
Calibration Std 3	3.0 µL		99.994 H_2O		3.0 µg/L
Calibration Std 4	6.0 µL		99.99 H_2O		6.0 µg/L
Calibration Std 5	10.0 µL		99.98 H_2O		10.0 µg/L
Calibration Std 6	20.0 µL		99.95 H_2O		20.0 µg/L
Calibration Std 7	50.0 µL		99.90 H_2O		50.0 µg/L
Calibration Std 8	100 µL		99.76 H_2O		100 µg/L
Calibration Std 9	0.250 µL		98.75 H_2O		250 µg/L
Surrogate Working Standard for Achon	0.5 mL of 10,000 mg/L		19.5 mL MeOH		250 µg/mL
Surrogate Working Standard for Centurion	0.5 mL of 10,000 mg/L		99.5 mL MeOH	100 mL	50 µg/mL
Internal Standard Working Standard for Archon	0.5 mL of 10,000 mg/L; 0.5 mL of 10,000 – 100,000 mg/L		19.5 mL MeOH	20 mL	250 µg/mL (1,4-dioxane-d8 is at 5000 µg/mL)
Internal Standard Working Standard for Centurion	0.5 mL of 10,000 mg/L; 0.5 mL of 10,000 – 100,000 mg/L		99.5 mL MeOH	20 mL	50 µg/mL (1,4-dioxane-d8 is at 5000 µg/mL)
Continuing Calibration Verification at 50ppb	100 µL of working standard	H_2O	199.9 mL H_2O	200 mL	50 µg/mL
Initial/Continuing Calibration Verification Standard at 20 ppb	50 µL of working standard	H_2O	249.95 mL H_2O	250 mL	20 µg/mL

Sample Preparation: Water samples are purged in the vial on the auto-sampler for SIM Analysis. The sample is prepared by adding 10mls of the sample using a 10ml syringe into a 40ml vial. All standards are treated in the same manner as the samples.

Suggested Purge Parameters: 6 minutes, 90 degrees heated purge at 120ml/mn

Attachment IX: Analytes using SIM acquisition for 8260B SIM/SCAN simultaneous acquisition

Analyte name	CAS Number	RL	acquisition method	Primary (Quant) Ion	Secondary (Qualifier) Ion
1,2,3-Trichloropropane	96-18-4	0.01	SIM	110	112
1,2-Dibromo-3-chloropropane	96-12-8	0.5	SIM	157	155
1,2-Dibromoethane (EDB)	106-96-4	0.05	SIM	107	109
1,2-Dichloroethane	107-06-2	0.2	SIM	62	98
1,4-Dioxane (p-Dioxane)	123-91-1	1	SIM	88	58
Carbon tetrachloride	56-23-5	0.05	SIM	117	119
cis-1,3-Dichloropropene	10061-01-5	0.4	SIM	75	77
Dibromochloromethane	124-48-1	0.4	SIM	129	127
Hexachloro-1,3-butadiene	87-68-3	0.2	SIM	225	227
trans-1,3-Dichloropropene	10061-02-6	0.4	SIM	75	77
Trichloroethene	79-01-6	0.05	SIM	130	132
Vinyl chloride	75-01-4	0.01	SIM	62	64

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STANDARD OPERATING PROCEDURE

PURGEABLE TOTAL PETROLEUM HYDROCARBONS IN WATER AND SOIL

Reference Methods: NWTPH-Gx

Local SOP Number:	S-MN-O-555-Rev.08
Effective Date:	Date of Final Signature
Supersedes:	S-MN-O-555-Rev.07

APPROVALS

Laboratory General Manager — Date: 29 Apr 2018

Laboratory Quality Manager — Date: 23 Apr 2018

PERIODIC REVIEW

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

Signature	Title	Date

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1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to define a purge and trap gas chromatographic method for analysis of total petroleum hydrocarbons/gasoline range organics (TPH/GRO) in ground water, wastewater, and solids.

2. Summary of Method

2.1. This method provides gas chromatographic conditions for the detection of volatile petroleum fractions such as gasoline and mineral spirits. Samples are analyzed utilizing purge and trap (P&T) sample concentration. Volatile organic compounds are volatilized by purging an inert gas; nitrogen or helium, through a 5 ml water sample. The vapor is then swept through a sorbent tube where the volatiles are trapped. When the purging is complete, the trap is heated and backflushed with inert gas to desorb the volatiles onto a chromatographic column. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID) for the GRO range.

3. Scope and Application

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

3.2. **Parameter**s: This SOP specifies the criteria for the identification and quantitation of volatile petroleum products. When the type of petroleum product is unknown, regular unleaded gasoline will initially be used as the default petroleum standard. The method is applicable for the identification, by pattern matching ("fingerprinting") and quantitation of volatile petroleum products, i.e. those petroleum products which the majority of the components elute within the gasoline range

4. Applicable Matrices

4.1. This SOP is applicable to ground water, wastewater, soils, and solids.

5. Limits of Detection and Quantitation

5.1. The reporting limit (LOQ) for all analytes is 100 ug/L for water and 5.0 mg/kg for soil in this method. All current MDLs are listed in the LIMS and are available by request from the Quality Manager.

6. Interferences

6.1. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of blanks provide information about the presence of contaminants.

6.2. Samples can be contaminated by diffusion of volatile organic compounds through the sample vial septum or between the vial and septum interface. A trip blank is prepared using HPLC grade, organic-free, water (or pre-tested, boiled DI water) and carried through the sampling and handling protocol or pre-tested, boiled, deionized water can serve as a check on such contamination. Trip blanks may also be purchased premade, refer to the Bottle Preparation SOP, S-MN-C-003, or equivalent replacement. Laboratory contamination is monitored by analyzing cooler blanks per SOP S-MN-Q-263, or equivalent replacement.

6.3. Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing of the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After analysis of a sample containing high concentrations of volatile organic compounds, one or more method blanks should be analyzed to

check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high concentrations of compounds being determined, it may be necessary to wash the purging device with methanol, rinse it with organic-free reagent water, and then dry the purging device in an oven less than 120°C. In extreme situations, the whole purge and trap device may require dismantling and cleaning, typically a methanol back flush followed by a DI water back flush. Screening the sample prior to analysis is recommended to prevent system contamination. This is especially true for soil and waste samples.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Table 7.1 – Sample Collection, Preservation, Shipment and Storage

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Aqueous samples are collected in 40mL capped vials (actual volume equals 42 mL with no headspace), and stored. The size of any bubble should be less than 5-6mm. Even though a minimal bubble is allowed, these vials should not be utilized unless no vials without headspace exist. If a vial is used that does have headspace, this should be footnoted in LIMS.	pH < 2 For volatiles, pH is measured after analysis and recorded in the daily sequence log. If the pH is greater than two, sample results must be flagged.	Above freezing but below 6°C	Must be analyzed within 14 days from collection A 7-day holding time from date collected is used if received unpreserved. If an improperly preserved sample was received, a comment must be added that shows up on the final report
Solid	Must be collected in soil VOA bottles with Teflon coated septum lined tops. They should be filled to the top to minimize headspace above the soil or they may be field preserved 1:1 with methanol in a tared vial.	n/a	Above freezing but below 6°C	Must be analyzed within 14 days from sample collection

8. Definitions

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

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

9.1. Table 9.1 – Equipment and Supplies

Supply	Description	Vendor/Item #/Description
Autosampler	Varian Archon 5100 and EST Archon 8100, Centurion w/s (or equivalent), or Atomx	Varian, Tekmar or Centurion
Sample Concentrator	EST Encon Envolution(EV) Concentrator, Tekmar Atomx, Tekmar (Lab Sample Concentrator) LSC 3100, LSC 3000, OI analytical Eclipse or equivalent	Encon, OI or Tekmar
Purging Chamber	The purging chamber is designed to accept 5mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap should be minimized. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3mm at the origin. The purge gas must be introduced no more than 5mm from the base of the water column	Encon,Tekmar, OI analytical or equivalent replacement

Traps	Trap Packing - A variety of traps are available from manufacturers. Any of these traps may be used if the trap packing materials do not introduce contaminants into the analysis and the data generated using the trap meets the initial and continuing calibration technical acceptance criteria of this method. Some traps used include, but are not limited to a tenax/silica gel/carbon trap, tenax/silica gel/carbon/OV-1 trap, and a Vocarb 3000 trap.	E7300-K03, EVO K trap E07300-L03, EVO MoRT trap Supelco 24920-u, Tekmar K traps for 3000/3100 Supelco 24910-U, Tekmar A traps for 3000/3100 14-9908-403, Strat-Trap, #9 (U-shaped) 14-9908-003, #9 Trap, straight trap H
Desorber	EST EV, Tekmar LSC-3100, LSC 3000 or equivalent should be capable of rapidly heating the trap to the manufacturer's recommended temperature for desorption, typically 180°C to 260°C, depending on the trap chosen	Encon, OI, Tekmar, or equivalent replacement
Gas Chromatograph	An analytical system complete with a temperature-programming	Agilent/Hewlett Packard 5890 or 6890, or equivalent replacement
Columns	30 m x 0.25 mm ID, 1.4 µm film thickness OR 30m x 0.53 mm ID, 1 mm film thickness 30m x 0.53 mm ID, 1 mm film thickness capillary column	RestekVMS-Rtx, DB-624 or equivalent replacement
Detectors	Temperature is set 10 to 20°C above the final oven temp to prevent condensation of sample in the detector. Ranges and lamp intensity are adjusted to provide appropriate sensitivity to achieve the MDL and linearity through the calibration range	O.I. 4450 PID/FID Tandem detectors or equivalent
Microsyringes	10 , 25, 50, 100, 250, 500, and 1000µL	Hamilton, or equivalent replacement
Syringes	5, 10, 25mL, 50 mL or gas-tight with shutoff valve	Hamilton, or equivalent replacement
Eppendorf Pipettor	1000µL	Eppendorf, or equivalent replacement
Balance	Analytical, 0.0001g, and top-loading, 0.1g	Denver Instrument
Glass Scintillation Vials	5 mL with Teflon lined screw-caps	Fisher Scientific C40131500 or equivalenet
Disposable pipettes	Glass pasteur pipettes	Fisher Scientific 13-678-31J or equivalent replacement
Volumetric Flasks	Class A - 5mL, 10mL, 25mL, 50mL, and 100mL, 200mL, 250mL, and 1000mL with ground-glass stoppers	Fisher Scientific or equivalent replacement
Spatula	Stainless steel	Fisher Scientific 14-357Q or equivalent replacement;
VOA vials	40 mL VOA Vials actual volume without headspace = 42 mL	C&G Unpreserved Vials NC9879693 or equivalent replacement;

10. Reagents and Standards

10.1. Table 10.1 – Reagents and Standards

Reagent/Standard	Concentration/Description	Requirements/Vendor/Item #
Organic-free Water (OFW)	De-ionized water	Verify that background levels of volatile compounds are acceptable by analysis
Methanol (MeOH)	CH_3OH - Fisher Purge and Trap grade or equivalent, demonstrated to be free of analytes. Store apart from other solvents	Fisher Scientific A453-1 or equivalent replacement
Stock Standard	Commercially purchased gasoline Stock Solution. Unleaded Gasoline Composite containing equal-weighted mixtures of	O_2Si or equivalent

	regular, plus and premium grades of commercial gasoline (O_2Si or equivalent) and should be certified as non-oxygenated gasoline.	
Intermediate	Using stock standard solutions, prepare the reagent in purge and trap grade methanol working standards containing GRO, either singly or mixed together. Working standards must be stored with minimal headspace at -10°C to -20°C and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Surrogate solution should be prepared every three months or sooner. If multiple mixes are used, the expiration date for the final solution MUST NOT exceed the earliest expiration date of any of the parents, or constituents.	O_2Si or equivalent
ICV Standard	Commercially purchased gasoline Stock Solution. Unleaded Gasoline Composite containing equal-weighted mixtures of regular, plus and premium grades of commercial gasoline and should be certified as non-oxygenated gasoline.	Restek
Surrogate Standards	Made from a stock solution of α,α,α -Trifluorotoluene(TFT). A working surrogate solution in methanol should be prepared at a concentration of 100µg/mL for α,α,α –TFT for waters and a 2500µg/mL of α,α,α –TFT for soils.	O_2Si or equivalent
Retention Time Marker	Commercially purchased; GRO retention marker solution is needed for both GRO and Washington VPH methods.	O_2Si or equivalent

10.1.1. Stock solutions - The ICV standard must meet the same criteria, but be from a different vendor or different source of raw materials, refer to S-MN-Q-275 or equivalent replacement for additional information.

10.1.1.1. After a portion of stock standard has been used, transfer any remaining stock standard solution into a clear bottle with a Teflon lined screw-cap or crimp cap vial or mini-inert valves. Store, with minimal headspace, at manufacturers listed conditions and protect from light. This unused portion is only good for 6 months from the date that the ampule is opened.

10.1.2. The surrogate standard may be combined into one mix for spiking samples if desired. Note the Centurion Autosampler is set to spike for 30 ms and the concentration of the working solution and surrogate solution need to be made at a lower concentration due to the fact that the Centurion Autosampler adds for 30 ms.

10.2. Table 10.2 - Working Standard Dilutions and Concentrations

Standard	Standard(s) Amount	Solvent	Solvent Diluent Volume	Final Total Volume	Final Concentration
Calibration standard intermediate	2.0 mL of 5000 µg/mL	MeOH	8.0 mL of MeOH	10.0 mL	1000 µg/mL
Calibration Std 1	1.0 µL	H_2O	99.999 H_2O	100 mL	10 µg/L
Calibration Std 2	2.5 µL		99.9975 H_2O		25 µg/L
Calibration Std 3	5.0 µL		99.995 H_2O		50 µg/L
Calibration Std 4	10.0 µL		99.99 H_2O		100 µg/L
Calibration Std 5	50.0 µL		99.95 H_2O		500 µg/L
Calibration Std 6	100 µL		99.90 H_2O		1000 µg/L
Calibration Std 7	250 µL		99.75 H_2O		2500 µg/L
Calibration Std 8	500 uL		99.50 H_2O		5000 ug/L
Surrogate Working Standard for Archon	0.5 mL of 10,000 mg/L	MeOH	19.5 mL MeOH	20 mL	250 µg/mL
ICV Standard at 1000 ppb	100 µL of working standard	H_2O	99.00 mL H_2O	100 mL	1000 µg/L
Continuing Calibration Verification Standard at 50 ppb	250 µL of working standard	H_2O	249.750 mL H_2O	250 mL	1000 µg/L

10.2.1. All standards, blanks, spikes, and samples must be analyzed using the same conditions. A set of at least five calibration standards containing the method analytes is needed (six standards are necessary for quadratic curve fits). One calibration standard should contain each analyte at a concentration at or below the reporting limit for that compound; the other calibration standards should contain analytes at concentration that define the range of the method.

10.2.2. To prepare a calibration standard, add an appropriate volume of standard solution to organic-free reagent water in a volumetric flask. Using a microsyringe, rapidly inject the standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared immediately before loading into the purge vessel. Transfer the contents to a purging device.

10.2.3. Refer to the Pace Analytical Quality Manual for initial calibration curve formulas.

10.3. Retention Time Window and Quantitation for TPH/GRO

10.3.1. Quantitation of TPH/GRO is performed by the external standard method. The concentration of Total Petroleum Hydrocarbon (TPH) or Gasoline Range Organics (GRO) in the sample is determined from a summation of the total response within the retention time window for TPH/GRO.

10.3.2. The retention time range (window) for gasoline integration must, at a minimum, include toluene through naphthalene. For other volatile petroleum products, the retention time window for integration must be adjusted to incorporate the majority of the components of the petroleum product(s) identified as present in the samples. If specific product identification can not be made, the analyst must quantitate the samples with the calibration curve of the petroleum product that most closely resembles that of the samples. The standard window is 0.1 minutes before toluene to 0.1 minutes after naphthalene.

10.3.3. The analyst shall use regular unleaded gasoline as the default petroleum product for reporting purposes when no petroleum products were identified in any initial screening or when the type(s) of petroleum products are unknown prior to analysis.

10.3.4. Integration must be "baseline to baseline" and is defined as a flat baseline drawn parallel to the x-axis of the chromatogram that includes all responses within the retention time window. The correct baseline placement would be a horizontal line drawn through the lowest point in the chromatogram. See Figure 1 for examples.

10.3.5. The calibration curve for TPH/GRO is built from the FID response of the appropriate standards at the varying concentrations listed in Table I. Response factors are calculated from the total area of the standards, using the external standard method of quantitiation (RF = AreaStd/AmtStd). The average RF from the initial calibration standard levels is used for quantitation of continuing calibration, QC and sample analyses.

10.3.5.1. For those surrogates that elute within the retention time range used for integration, the area of the surrogate will be included in all standards and samples have surrogate added at equal concentration to yield the appropriate area of the petroleum product.

10.3.6. Refer to the Pace Analytical Quality Manual for initial calibration curve formulas.

10.3.7. Surrogates are spiked into the sample utilizing the autosampler using a single point calibration for water and maybe be use for medium level soils. Alternatively for medium level soils, a multipoint surrogate curve maybe employed and the surrogate solution is spiked during preparation stage of the soil sample.

11. Calibration and Standardization

11.1. Table 11.1 – Calibration and Standardization

Calibration Metric	Parameter/Frequency	Criteria	Comments
Calibration Curve Fit	Linear Regression	$r \geq 0.99$	If not met, try non-linear regression fit. If still not met, remake standards and recalibrate and

	Non-linear Regression	COD ≥ 0.99 % RSD ± 15 No individual standard may vary from true value by more than 15%	verify before sample analysis.
Second Source Verification Standard (ICV)	Immediately after each initial calibration	% Diff ± 20	If the requirements for ICV are not met, verify the standard preparation, and determine if there are any apparent issues with the initial analysis. Reanalyze one more time. Only two injections of the ICV are permitted prior to recalibrating the instrument.
Continuing Calibration Verification (CCV) – See section 11.2	Prior to the analysis of any samples and after every 20 samples thereafter. Samples must be bracketed with a closing CCV standard: analyze CCV standard near a midpoint level of calibration curve.	% Diff ± 20	If a CCV falls to meet the require %RSD, attempt to correct the problem: If the first CCV fails, determine the root cause for the failure which may include bad CCV solution, bad spike of CCV standard, standard mix degradation, analytical system not conditioned, active sites and/or cold sites in the trap or concentrator, contaminated system due to dirty samples, or analytical conditions changed over time. Corrective actions will be case by case depending on the root cause, but may include: making a new CCV solution, running a different vial of a CCV solution, using a different standard to make the CCV solution, making new standards and new CCVs, baking out the concentrator, or replacing transfer lines on concentrator. Recalibrate the system if major maintenance is required. If the second CCV fails, a new initial calibration curve must be prepared before samples can be reported. Alternate criteria may be applied on a client or program specific basis.
RL Verification	The State of MN requires the RL to be verified upon ICAL and every 30 days.	RL must be ± 40% of the true value	If the RL verification doesn't meet the criteria, evaluate the data quality objectives to determine if the RL can be raised – contact QA to adjust the RL or re-calibration

11.2. Daily Calibration/Continuing Calibration Verification (CCV)

11.2.1. For waters, the CCV and LCS/LCSD solutions are the same solution (prepared the same, using the same standards, etc.). The CCV and LCS/LCSD analyses are interchangeable and can be used for both sample types (the CCV can also be used as the LCS and the LCS can also be used as the CCV) provided that 2 CCVs didn't already fail in a row (which would trigger an initial calibration). When these analytical runs are used as the same file, they should be named as 2 separate files to distinguish the sample types for reporting the appropriate reports and so that there is a unique file name associated with each sample type.

11.2.2. For medium level soils, LCS/LCSDs are not interchangeable with the CCVs in the run sequences as the LCS/LCSDs are prepared and extracted with the associated sample on the day of preparation while the CCVs and initial calibration solutions are prepared by using a ratio of 1 mL methanol into 50 mL of DI water (to matrix match the calibrations to the sample matrix) and are not extracted.

11.2.3. Alternate criteria may be applied on a client or program specific basis. Any requirement outlined in Quality Assurance Project Plans (QAPPs) will supersede these criteria.

12. Procedure

12.1. GC analysis

12.1.1. Water samples

12.1.1.1. Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Screening can be accomplished by using a headspace GC PID or by analyzing the sample at a dilution by GC.

12.1.1.2. The sample vial is placed into the autosampler tray and the Archon 5100 or EST 8100, or equivalent Autosampler spikes the surrogate (SS) mix. If a dilution is required, the necessary sample volume is manually diluted and placed into the Autosampler.

12.1.1.3. The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample vial is sealed.

12.1.1.3.1. Dilutions may be made in volumetric flasks of various sizes. Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

12.1.1.3.2. Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask. See table III for common dilution factors.

12.1.1.3.3. Inject the proper aliquot of sample into the flask. Dilute the sample to the mark with organic-free reagent water. Cap the flask and invert three times. Once sample dilution is completed, the pH of the sample must be taken with pH paper. If the pH is greater than 2 the sample must be footnoted. Repeat above procedure for additional dilutions.

12.1.1.3.4. Fill the vial with diluted sample and load onto the autosampler.

12.1.1.4. The autosampler adds the spiking solution and the surrogate spiking solution to the 5mL sample aliquot. The amount added by the autosampler should be equivalent to the concentration of 20 µg/L of the surrogate.

12.1.1.5. Analyze the samples using the same autosampler and GC conditions used to pass initial calibration, CCV standard, and blank criteria.

12.1.1.6. If the initial analysis of sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated peaks, this analysis must be followed by a blank organic-free reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences. Alternately, samples loaded on an autosampler can be accepted after a subsequent sample is shown to be free of carry-over contamination or if the detection is 10x greater than the carryover detection. Carryover in P&T systems can vary for instrument to instrument depending on the condition of the equipment. Analysts must review the carryover after the upper level of the initial calibrations and after the ICV, in addition they monitor the carryover daily on the system blanks ran which is generally ran after QC samples. It is common for the laboratory to run multiple blanks after an initial calibration to monitor the carryover and ensure the ICV does not have carryover affecting the % recoveries. Daily, it is common for the laboratory to run a system blank before the method blank. This is to help determine if there is a contamination coming from the system itself or if contamination occurred during the sample preparation phase.

12.1.1.7. All samples with detections and subsequent injections must be thoroughly reviewed for potential carryover contamination of GRO and PVOCs to ensure low-level carryover is not occurring into subsequent analyses.

12.1.1.8. For matrix spike analysis, add 42µL of a 1000µg/mL working standard solution to the aqueous sample vial (42 mL actual volume). This is the equivalent to a concentration of 1000 µg/L of each matrix spike standard. Add the spiking solution through the septa of the vial as the vial should not be opened to maintain sample integrity.

12.1.1.9. All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the calibration range.

12.1.1.10. Once sample analysis is completed, the pH of the sample must be taken with pH paper and recorded in the instrument run logbook. If the pH is greater than 2 the sample must be footnoted.

12.1.2. Sediment/soil and waste samples - For medium level soils (MLS) the Pace label is placed on all containers during the log-in process which is performed by sample receiving. The weight of the label is subtracted from all soil samples to reflect the weight of the soil weight. The weight of the label is determined annually (unless specified) by weighing out 10 labels and determining an average weight. This subtracting of the label weight is performed in the soil prep logbook. It is recommended that all samples of this type be screened prior to analysis. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and trap system, and require extensive cleanup and instrument downtime.

12.1.2.1. A sample is either extracted or diluted with methanol, depending on its solubility. An aliquot of the extract is added to organic-free reagent water. This is purged at ambient temperature.

12.1.2.2. **NOTE: The following steps must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.**

12.1.2.3. To prepare the laboratory method blank, laboratory control sample(LCS) and laboratory control sample duplicate(LCSD) weigh out 10 grams of Ottawa sand and add 10mL of methanol to a 40 mL VOA vial (42 mL actual volume). The weight of the BLK, LCS, and LCSD is record as 10 grams so long as the actual weight is 10+/- 0.1grams. They should be uniquely labeled by QC batch numbers to ensure they are analyzed with the correct batch of samples. The LCS/LCSD are also spiked with the 100µL of 5000 µg/mL of the working standard to achieve a final concentration of 1000 µg/L after the 1:50 dilution, or spiked with 200µL of 2500 µg/mL of the working standard to achieve a final concentration of 1000 µg/L. And 10 µL of 2500 µg/mL of α,α,α -Trifluorotoluene(TFT) working standard may be spiked into the samples to monitor the extraction process.

12.1.2.4. To prepare the matrix spike (MS) and matrix spike duplicate (MSD), weigh the vial and record the weight to the nearest 0.01g. Subtract the vial weight prior to sampling and record the final weight. If the weight is greater than the expected 5g, 10g, or 25g weight, the addition of methanol is necessary in order to maintain the 1:1 sample to solvent ratio. Add the appropriate amount of 5000 ug/mL working standard, or 2500 µg/mL working standard to achieve a final concentration of 1000 µg/mL after the 1:50 dilution. The appropriate amount of 2500 µg/mL of α,α,α -Trifluorotoluene(TFT) working standard may be added to achieve a final concentration of 50ug/L after the 1:50 dilution. If insufficient sample volume was received to prepare the MS/MSD, the project should be footnoted and the project manager must be notified.

12.1.2.5. To prepare samples that arrive preserved in methanol, weigh the vial and record to the nearest 0.01g. Subtract the vial weight prior to sampling and record the final weight. If the weight is greater than the expected 5g, 10g, or 25g weight, the addition of methanol is necessary in order to maintain the 1:1 sample to solvent ratio. If the weight is less than expected 5g, 10g or 25g weight, record the difference and in the soil prep logbook and EPIC Pro prep batch.

12.1.2.6. To prepare samples that are not preserved in methanol the sample consists of entire contents of sample container. Using a top-loading balance, weigh 10 grams (wet weight) of the

sample into a tared 40 mL vial. Record the weight to 0.01g. Quickly add 10 mL of methanol. Samples not field preserved should be preserved within 48 hours of collection as per specific client technical specifications. Client, QAPP, or state requirements may supersede this requirement.

12.1.2.7. Oily, solid waste or product samples are generally not field preserved due to the unknown solubility. If the sample is not soluble in water, a waste dilution will be performed by weighing out 1gram of the sample into a tared 40mL VOA vial. Record the weight to 0.01 grams.

12.1.2.8. The LCS/LCSD, MS/MSD, method blank, and all associated samples within the batch must be shaken for a minimum of 1 minute, then sonicated for a minimum of 2 minutes. After sonicating, prepare the samples by adding 1000 µL either by syringe or eppendorf pipetter of the methanol extract to a 50 mL volumetric flask containing DI water. Dilute to a final volume of 1:50 using DI water. Fill a 40 mL VOA vial with the prepared sample for analysis.

12.1.2.9. The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample vial is sealed.

12.1.2.9.1. Dilutions may be made in volumetric flasks of various sizes. Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

12.1.2.9.2. Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask. See table IV for common dilution factors.

12.1.2.9.3. Inject the proper aliquot of sample extract into the flask and the proper amount of P&T methanol, so that the same amount of methanol is added to all samples and QC. Dilute the sample to the mark with organic-free reagent water. Cap the flask and invert three times.

12.1.2.10. For storage, transfer a portion of the extract into a 2 mL glass autosampler vial, with a Teflon-lined cap, minimizing the headspace and store in a freezer for no longer than one week prior to analysis.

13. Quality Control

13.1. Table 13.1 – Quality Control

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water	One per 10 samples or less	Target analytes must be free of contamination to half the reporting limit. If results are reported to MDL, target analytes in MB should be non-detect	Re-analyze all samples. ***Exceptions:*** If sample ND, report sample without qualification; If sample result >10x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier indicating blank contamination; If sample result <10x MB detects, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition. If there is insufficient sample volume B flag the detections present in the samples associated with the contaminated blank.

Laboratory Control Sample (LCS)/ Laboratory Control Spike Duplicate (LCSD)	DI water spiked with all target compounds For water batches, the CCV and LCS can be the same solution; the CCV qualifies for a LCS or LCSD	One per 20 samples; the LCS must run at the beginning of a batch and the LCSD at the end of the batch.	%RPD ≤ 20 Internally generated limits which are updated annually. See LIMS for current limits.	Evaluate the LCS to determine the cause of the outlier; verify calculation and standard preparation. Perform any necessary system maintenance prior to reanalyzing the LCS. For water, the LCS is the same solution as the CCV: the associated samples will have to be reanalyzed accordingly. ***Exceptions:*** If LCS recovery is > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)/ Matrix Sample Duplicate (MSD)	Client sample spiked with all target compounds	One per 20 samples if there is sufficient sample volume per client requests Performed when > 3 containers (except soil received in packed jars) have been received to ensure that sufficient sample remains for any re-analysis (i.e., dilutions, instrument problems). An MS and sample duplicate (DUP) must be analyzed if insufficient sample is received and data footnoted	%RPD ≤ 30 Internally generated limits which are updated annually. See LIMS for current limits.	If there is an outlier, the corresponding laboratory control spikes must be evaluated. If the same outlier occurs in the LCS, a system problem may be assumed. In this instance, samples may have to be reanalyzed. If the LCS reports an acceptable recovery, matrix interferences are assumed. In either instance, the data on the final report must be footnoted with the outliers and possible reason if known; Client, QAPP, or state requirements may supersede this. For Minnesota Admin Contract clients – all MS/MSD failures require reanalysis of the MS/MSD and the original sample. If it is still out of control, investigate and document the cause in the associated narrative as well as qualifying appropriately.
Duplicate	Sample Dup	One per 10 samples	%RPD ≤ 30%	Report results with an appropriate footnote.
Surrogate	α,α,α - Trifluorotoluene	All samples and QC samples must be evaluated for surrogate % recoveries.	% Rec: 50-150%	If recovery is not within limits, check any errors in the calculations and surrogate solution. Check instrument performance and re-analyze the sample when the problem is identified. If problem is not identified, re-analyze the sample. If surrogate recovery is high due to matrix, determine if the sample needs to be re-run. If the reanalysis is still not within the limits, report the initial run and footnote appropriately. If the recovery is now within limits, report the second run (if within holding time). ***Exception:*** If surrogate recovery is high and all associated analytes of interest are non-detect (a positive bias), the sample does not need to be re-run. Flag the data with the appropriate footnote.

14. Data Analysis and Calculations

14.1. The concentration of gasoline in aqueous samples is calculated utilizing the following equation:

Equation 1: Gasoline Concentration Equation

$$Amount_{(y)} = \frac{\left(Area_{(y)}\right)\left(DF\right)}{\left(RF_{(y)}\right)}$$

Where:

y	=	Any calibrant peak or group of peaks
$Area_{(y)}$	=	peak area of y in the sample
DF	=	Dilution factor
$RF_{(y)}$	=	The response factor for peak y
Amount	=	Concentration of *y* in the sample (µg/L)

Equation 2: Mid-Level Gasoline Concentration

$$\text{Equation Medium Level Conc(y) } (mg/kg) = \left[\frac{\left(A_y\right)\left(DF\right)\left(V_t\right)}{\left(RF_{(y)}\right)\left(W_s\right)}\right] \bullet 50$$

Where:

y	=	Any calibrant peak or group of peaks
$A_{(y)}$	=	Peak area of y in the sample
DF	=	Dilution factor
$RF_{(y)}$	=	The response factor for peak y
V_t	=	Volume of total extract (mL)
W_s	=	Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

Note: All methanol extracts are diluted 1:50.

Note: Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The percent dry weight of the sample should be reported along with the data in either instance.

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See tables in section 11 & 13.

16. Corrective Actions for Out-of-Control Data

16.1. See tables in section 11 & 13.

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

17.1. If not specifically listed in the tables in section 11 & 13, the contingencies are as follows. If there is no additional sample volume to perform re-analyses, all data will be reported as final with applicable qualifiers. If necessary, an official case narrative will be prepared by the Quality Manager or Project Manager.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. **Method Detection Limit (MDL**) Study: An MDL study must be conducted annually (per the method) per S-MN-Q-269 – Determination of Limit of Detection and Limit of Quantitation (or equivalent replacement) for each matrix per instrument.

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-MN-Q-279 - Training and Employee Orientation (or equivalent replacement).

18.4. Periodic **performance evaluation (PE)** samples are analyzed to demonstrate continuing competence per SOP S-MN-Q-258 – Proficiency Testing Program (or equivalent replacement). Results are stored in the QA office**.**

19. Method Modifications

19.1. The laboratory uses 10 g per 10 mL methanol

19.2. Surrogate uses are included in standards and samples following EPA Method 8015B and 8015C.

19.3. Prepared soil samples stored in client provided preserved VOA bottle. For unpreserved containers, storage occurs in 40mL VOA vial used for sample preservation. Vials are stored in temperature greater than freezing but below 6ºC.

20. Instrument/Equipment Maintenance

20.1. Please refer to the GC 5890 instrument manual for maintenance procedures performed by the lab.

20.2. All maintenance activities are listed daily in maintenance logs that are assigned to each separate instrument.

21. Troubleshooting

21.1. The purge and trap concentrator must be leak free in order to ensure properly sample purge efficiency and desorption. If analyst notices significant decrease in response and suspects a possible leak, one can leak check the concentrator to ensure the P&T concentrator is free for leaks. This can be done through the software or manually by capping the vent valve of the concentrator and purging a blank.

22. Safety

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

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

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in S-MN-S-003 - Waste Handling and Management (or equivalent replacement).

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

24. Pollution Prevention

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

25. References

25.1. NWTPH-Gx, "Volatile Petroleum Products Method for Soil and Water"

25.2. SW-846, Vol IB, "Nonhalogenated Volatile Organics by Gas Chromatography," Method 8015C, Revision 3, Feb 2003

25.3. SW-846, Vol IB, "Nonhalogenated Volatile Organics by Gas Chromatography," Method 8015B, Revision 2, Dec 1996

25.4. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Update III, Method 8000B

25.5. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 4rd Edition, Final Update IV, Method 8000C

25.6. "Method 524.3 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Rev. 1.0" Technical Support Center Office of Ground Water and Drinking water, U.S. Environmental Protection Agency, Cincinnati, Ohio, June 2009

25.7. Pace Quality Assurance Manual- most current version.

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

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

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Table I: THC/GRO Calibration Curve

26.2. Table II: Practical Quantitation Limits

26.3. Table III: Common Dilution Factors for Waters

26.4. Table IV: Common Dilution Factors for Soils

26.5. Attachment I: Example of NwTPH Integration

27. Revisions

Document Number	Reason for Change	Date
S-MN-O-555-Rev.08	Updated LLC Removed "uncontrolled" Added "Copies without a distribution number below are considered uncontrolled" to the statement of copyright. General formatting. 10.1.1 – updated SOP reference to local SOP 12.1.1.2 – removed "Archon 5100 or EST 8100" 12.1.1.4 – removed "Note the centurion….autosampler." 12.1.1.6 – added "must" 12.1.1.7 – added "with detections and subsequent injections" and "for potential carryover contamination of", removed "when sample concentrations exceed" and "detection of 500ug/L and 50 ug/l" Table 13.1 – changed MS/MSD frequency to DUP "must be analyzed" instead of "will be", also added "and data footnoted. Duplicate row component column- removed "MSD or LCSD" Section 14.1 "sedment" changed to "sediment" Replaced reference to corporate training SOP with local SOP S-MN-Q-279 in Section 18.3. Table I updated to TPH instead of THC.	11Apr2018

TABLE I

TPH/GRO Calibration Curve (ug/L)

Cal Levels	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
TPH/GRO concentra	10	25	50	100	500	1000	2500	5000

TABLE II

Practical Quantitation Limit (PQL)

Component	**PQL**
TPH/GRO in soil	5.0 (mg/Kg)
TPH/GRO in water	100 ug/L

TABLE III Common Dilution Factors for Waters

Water Dilution Factors		
Dilution	**Into 50 mL**	**Into 100 mL**
2x	25 mL	n/a
5x	10 mL	20 mL
10x	5 mL	10 mL
20x	2.5 mL	5 mL
25x	2 mL	4 mL
50x	1000 uL	2 mL
100x	500 uL	1000 uL
200x	250 uL	500 uL
500x	100 uL	200 uL
1000x	50 uL	100 uL
10000x	5 uL	10 uL

Table IV: Common Dilution Factors for Soils

Soil Dilutions into 50mLVolumetric		
Dilution Factor	Volume of Soil Extract (uL)	Volume of P&T Methanol (uL)
1	1000	0
2	500	500
5	200	800
10	100	900
20	50	950
25	40	960
50	20	980
100	10	990
200	5	995
500	2	998
1000	1	999
Beyond 1000x Serial Dilutions are performed.		

Soil Dilutions into 100mLVolumetric		
Dilution Factor	Volume of Soil Extract (uL)	Volume of P&T Methanol (uL)
1	2000	0
2	1000	1000
5	400	1600
10	200	1800
20	100	1900
25	80	1920
50	40	1960
100	20	1980
200	10	1990
500	4	1996
1000	2	1998
Beyond 1000x Serial Dilutions are performed.		

ATTACHMENT I - Example of NwTPH Integration

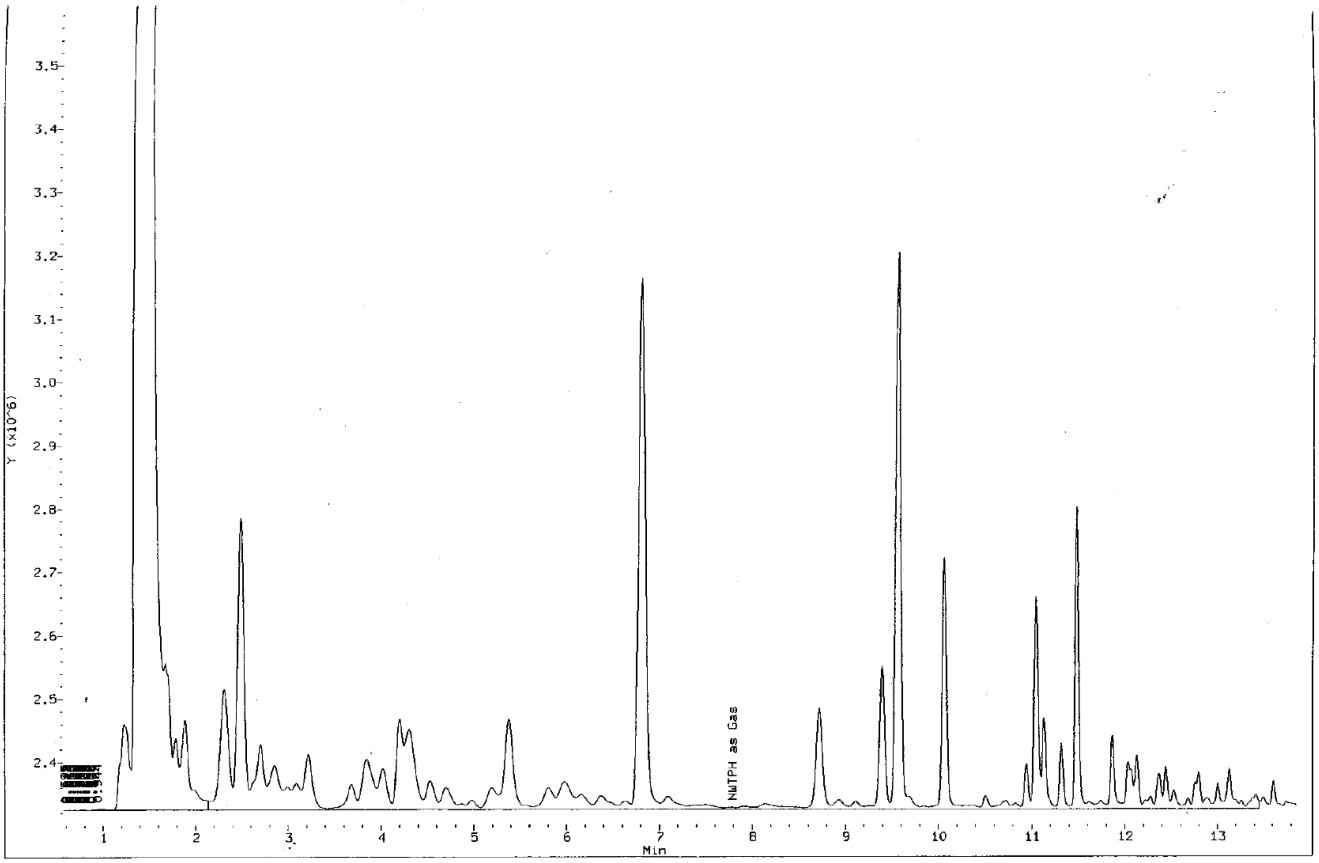

Figure 1. Example chromatography of "baseline to baseline" integration drawn parallel to the axis of the chromatograph that includes all responses with the retention time window. The typical retention time window for NWTHP-Gx is 0.1 minutes before toluene and 0.1 minutes after naphthalene.

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STANDARD OPERATING PROCEDURE

THE DETERMINATION OF DIESEL RANGE ORGANICS, RESIDUAL RANGE ORGANICS AND TOTAL EXTRACTABLE HYDROCARBONS

Reference Methods: 8015B/C/D, AK102, AK103 and NwTPH-Dx

Local SOP Number:	S-MN-O-578-rev.08
Effective Date:	Date of Final Signature
Supersedes:	S-MN-O-578-rev.07

APPROVALS

Laboratory General Manager — Date: 01 Aug 2018

Laboratory Quality Manager — Date: 01 Aug 2018

PERIODIC REVIEW

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

Signature	Title	Date
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SECTION **PAGE**

1. Purpose/Identification of Method

1.1. The purpose of this Standard Operating Procedure (SOP) is to provide instructions on the procedures for extraction and analysis of samples by Methods 8015B, 8015C, and 8015D, AK102, AK103 and NwTPH-Dx.

2. Summary of Method

2.1. This SOP describes the procedure for 8015, AK 102 and AK 103. The SOP is combined since it is possible for these methods to utilize the same surrogates, calibration solutions, and calibration levels. The only variation in the methods is the carbon ranges selected for each individual method which can be integrated separately from the same analytical runs.

2.2. Water Samples – 250 mL for AK102, AK 103 and NwTPH and 500mL for 8015. Samples are extracted at a pH <2 with methylene chloride in a separatory funnel. The extract is dried and concentrated; then, analyzed using a gas chromatograph coupled with a flame ionization detector (FID).

2.3. Soil Samples – A 10 g soil sample is mixed with anhydrous sodium sulfate (sufficient to make free-flowing) for probe sonication. An aliquot of solvent is added and extracted using an ultrasonic disrupter. This procedure occurs three times in succession and then the extract is concentrated to 1 mL. A portion is analyzed using a gas chromatograph coupled with a flame ionization detector (FID).

3. Scope and Application

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

3.2. **Parameters**: This SOP applies to organic carbon ranges that begin at C10 to C40.

3.3. The carbon ranges for the appropriate method are listed below. In all methods, Diesel Fuel #2 is used for the calibration range for the diesel component range, and a mixture of SAE 30 and SAE 40 weight motor oil is used for the calibration for the motor oil/oil range organics component range.

3.3.1. Method AK 102 is designed to measure petroleum products that elute in the carbon range from the beginning of C10 to the beginning of C25 (represented by Commercial #2 Diesel Fuel in calibration curves) and is reported as Diesel Range Organics or DRO. The AK 103 method is designed to measure petroleum products that elute in the carbon range from the beginning of C25 to the end of C36 (represented by a mixture of SAE 30 and SAE 40 motor oils in calibration curves), and it is reported as Residual Range Organics or RRO.

3.3.2. 8015 is designed to measure petroleum products in the diesel and oil range. Diesel range organics (DRO) measures petroleum products that elute in the carbon range from the beginning of C10 to the end of C28. The oil range organics component of the method is designed to measure petroleum products that elute in the carbon range from the beginning of C24 to the end of C36. A total C10-C36 range is also included in this method.

3.3.3. NwTPH-dx is designed to measure the petroleum products that elute in the carbon range from the beginning of C12 to the end of C24, which are reported as Diesel Range, as well as Petroleum products that elute in the carbon range from the end of C24 to the end of C40 which are reported as Motor Oil Range. If requested by the client the NwTPH-dx method is also capable of reporting kerosene, gasoline, fuel #6, mineral spirits and hydraulic fluid.

4. Applicable Matrices

4.1. This SOP is applicable to water and solid matrices.

5. Limits of Detection and Quantitation

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

6. Interferences

6.1. Other organic compounds including animal and vegetable oil and grease, chlorinated hydrocarbons, phenols, phthalate esters and biogenic terpenes will contribute to the DRO detection in AK 102.

6.2. The petroleum patterns used in both AK102 and AK103 overlap with each other slightly, meaning that heavy petroleum products such as lubricating oil and crude oils can cause a response in the AK102 method and visa versa due to the nature of "baseline to baseline" integrations in these methods.

6.3. Scrupulous cleaning of glassware and other equipment is necessary to avoid contamination and carryover. Glassware, sonicator probes, and other items used in sample preparation should be thoroughly detergent washed, rinsed with tap water and distilled water, solvent rinsed, and dried prior to use. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

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

6.5. Potential exists for extracts to carry-over from sample to sample on the instrumentation especially when working with heavy petroleum patterns.

7. Sample Collection, Preservation, Shipment and Storage

7.1. Table 7.1 Sample Collection, Preservation and Storage.

Sample type	Collection per sample	Preservation	Storage	Hold time
Aqueous	Amber glass with Teflon-lined screw cap lids: 250 mL for AK102, AK 103 and NwTPH and 500mL for 8015. Allow additional aliquots for matrix spike and matrix spike duplicate samples.	Acidified with 1:1 hydrochloric to pH<2; no headspace	<6°C but above freezing	Must be extracted within 14 days of collection and analysis within 40 days of extraction. For NwTPH if not acidified holding time is 7 days. 8015 hold time is 7 days for preserved and unpreserved samples.
Solids	4 or 8 oz wide mouth amber glass jars with Teflon-lined lids	Thermal only	<6°C but above freezing	Must be extracted within 14 days of collection and analysis within 40 days of extraction.

8. Definitions

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

8.2. Ranges definition can be found in Attachment I.

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

9.1. Table 9.1 Equipment and Supplies.

Supply	Description	Vendor/ Item # / Description
Separatory Funnels	2-L with Teflon stopcock	Fisher Scientific 10-437-25E or equivalent vendor
Erlenmeyer flasks	250 mL	Fisher Scientific 07250090 or equivalent vendor
Erlenmeyer flasks	500 mL	Fisher Scientific 07250091 or equivalent vendor
pH indicator paper	0-14	Fisher Scientific 09-876-17 or equivalent vendor
Funnels	Stainless Steel	Fisher Scientific 10-368B or equivalent vendor
Glass wool	n/a	Fisher Scientific 11-388 or equivalent vendor
Sodium Sulfate	Baked – See S-MN-500, or equivalent replacement	Fisher Scientific S415-200LB or equivalent vendor
Balance	Top loading that can accurately weigh to the nearest 0.01 g.	Denver instrument or equivalent replacement
Sonicator	Equipped with ¾" horn	Misonix or equivalent replacement
Beakers	400 mL	Fisher Scientific 07250057 or equivalent vendor
Stainless steel utensil	Scoopula	Fisher Scientific 14-357Q
Kuderna-Danish (KD) Apparatus	10 mL Concentrator tubes and 500 mL evaporation flasks with connecting clamps	Fisher Scientific 192002AP2 or equivalent vendor
Snyder Column	3 ball macro	Fisher Scientific 192002AP1 or equivalent vendor
Boiling chips	Beads or chips that are solvent rinsed	Fisher Scientific 02215521 or equivalent vendor
Water bath	Heated with concentric ring covers in a hood – set to 80-90 °C	Custom made
Pipettes	Disposable 1 mL serological pipettes	Fisher Scientific 13-678-31E or equivalent vendor
Pasteur Pipettes	5 ¾ inch	Fisher Scientific 13-678-20B or equivalent vendor
20 mL vial	With screw cap	Fisher Scientific 03-339-21J or equivalent vendor
Gas Chromatograph (GC)	With Flame Ionization Detector (FID)	Hewlett-Packard 6890N with 7683 Autosampler, or equivalent
GC Column	Semivolatiles, 0.25 µm film thickness, 30 m x 0.32 mm ID, or equivalent replacement	Phenomenex 7HG-G027-17
Metal measuring device	Use for measuring volume of water	N/A
Graduated Cylinder	Use for measuring volume of water; 500 mL	Fisher Scientific 12-141-329 or equivalent
Chemstation	Data Acquisition software	Chemstation, see master software list for version
Target	Data Processing software	Target, see master software list for version
Horizon	Data Reporting Software	Horizon, see master software list for version
Gandalf	Data packaging software	In house software

10. Reagents and Standards

10.1. Table 10.1 Reagents and Standards.

Reagent/Standard	Concentration/ Description	Requirements/ Vendor/ Item #
Organic-free Water (OFW)	De-ionized water	Verify that background levels of volatile compounds are acceptable by analysis
Methylene Chloride	MeCl, Optima grade or equivalent	Fisher Scientific D151-4 or equivalent
Acetone	Optima grade or equivalent	Fisher Scientific A929-4 or equivalent
Sand	Demonstrated to be analyte-free	Menards or equivalent
Hydrochloric Acid	1:1 HCl prepared by adding equal amounts of concentrated HCl to DI water	Fisher Scientific A508-P212 or equivalent
Silica Gel	60-100 mesh pre-activated	Supelco 236799-1KG or equivalent
Surrogate	O-Terphenyl 2000 ug/mL	Accustandard DRO-AK-102-SS-10x-PAK
Surrogate	n-Triacontane d62 5000 ug/mL	Accustandard DRO-SS
Matrix Spike/Ical	Diesel Fuel #2 50,000 ug/mL	Restek 31258
Matrix Spike/Ical	Residual Range Calibration Std. 50000ug/mL	Restek 31817
Initial Calibration Verification	SAE 30W Motor Oil 20,000 ug/mL	Accustandard FU-18-D-40x
Initial Calibration Verification	SAE 40W Motor Oil 20,000 ug/mL	Accustandard FU-19-D-40x
Initial Calibration Verification	#2 Fuel Oil 20,000	Accustandard FU-002-D-40x
Retention Time Marker	Decane(C10), Dodecane(C12), Tetracosane(C24), Pentacosane(C25), Octacosane(C28), Hexatricontane(C36) and Tetracontane(C40) at 5000 ug/mL	O_2Si 117300-01 or equivalent
Kerosene	20,000 ug/mL	Accustandard FU-005-D-40X or equivalent
Gasoline	20,000 ug/mL	Accustandard GA-001-40X or equivalent
Fuel #2	20,000 ug/mL	Accustandard FU-008-D-40X or equivalent
Mineral Spirits	20,000 ug/mL	Accustandard HS-0025-D-40X or equivalent
Hydraulic Fluid	20,000 ug/mL	Accustandard FU-020-D-40X or equivalent
Kerosene Initial Calibration Verification	5000 ug/mL	Restek 31094 or equivalent
Gasoline Initial Calibration Verification	5000 ug/mL	Restek 30096 or equivalent
Fuel #6 Initial Calibration Verification	5000 ug/mL	Restek 31218 or equivalent
Mineral Spirits Initial Calibration Verification	5000 ug/mL	Restek 31225 or equivalent
Kerosene Initial Calibration Verification	50000 ug/mL	Restek 31839 or equivalent

10.2. All standards are stored according to the manufacturer specifications prior to opening. Once opened, remaining aliquots will be stored according to manufacturers' specifications and will be given and expiration date of 1 year. If the manufacturer's expiration date is sooner than 1 year, it must be utilized prior to the expiration date.

10.3. Working Standard Dilutions and Concentrations

10.3.1. Initial Calibration Stock

Standard	Standard(s) Amount	Solvent	Solvent Volume	Final Total Volume	Final Concentration
O-Terphenyl	1.0 mL	Methylene Chloride	2.8 mL	5.0 mL	400 ug/mL
n-Triacontane d62	0.400 mL				400 ug/mL
Diesel Fuel #2	0.400 mL				4000 ug/mL
Residual Range calibration standard	0.400 mL				4000 ug/mL

10.3.2. Initial Calibration

Standard	Standard (s) Amount	Solvent	Solvent Volume	Final Total Volume	Final Concentration	RRO + Diesel Fuel #2 Conc. (C10-C36)
Calibration Std 1	Calibration Std 2 0.6 mL	Methylene Chloride	0.400 mL	1.0 mL	0.6/6 µg/mL	12 µg/mL
Calibration Std 2 Make 2 vials (used to make calibration Std. 1)	Calibration Std 4 0.200 mL	Methylene Chloride	0.800 mL	1.0 mL	1.0/10 µg/mL	20 µg/mL
Calibration Std 3	Calibration Std 4 0.500 mL	Methylene Chloride	0.500 mL	1.0 mL	2.5/25 µg/mL	50 µg/mL
Calibration Std 4 Make 2 vials; each vial used to make level 2 and 3)	ICAL Stock 0.0125 mL	Methylene Chloride	0.9875 mL	1.0 mL	5/50 µg/mL	100 µg/mL
Calibration Std 5	ICAL Stock 0.025 mL	Methylene Chloride	0.975 mL	1.0 mL	10/100 µg/mL	200 µg/mL
Calibration Std 6	ICAL Stock 0.050 mL	Methylene Chloride	0.950 mL	1.0 mL	25/250 µg/mL	500 µg/mL
Calibration Std 7	ICAL Stock 0.125 mL	Methylene Chloride	0.875 mL	1.0 mL	50/500 µg/mL	1000 µg/mL
Calibration Std 8	ICAL Stock 0.250 mL	Methylene Chloride	0.750 mL	1.0 mL	100/1000 µg/mL	2000 µg/mL
Calibration Std 9	ICAL Stock 0.500 mL	Methylene Chloride	0.500 mL	1.0 mL	200/2000 µg/mL	4000 µg/mL
Calibration Std 10	ICAL Stock 1.0	NA	NA	1.0 mL	400/4000 µg/mL	8000 µg/mL

10.3.3. Initial Calibration Verification

Standard	Standard(s) Amount	Solvent	Solvent Volume	Final Total Volume	Final Concentration	RRO + Diesel Fuel #2 Conc. (C10-C36)
n-Triacontane d62	.010 mL	Methylene Chloride	0.915 mL	1.0 mL	50/500 ug/mL	1000 µg/mL
O-Terphenyl	0.025 mL					
#2 Fuel oil	0.025 mL					
SAE 30W Motor Oil	0.0125 mL					
SAE 40W Motor Oil	0.0125 mL					

10.3.4. Matrix Spike

Standard	Standard(s) Amount	Solvent	Solvent Volume	Final Total Volume	Final Concentration	RRO + Diesel Fuel #2 Conc. (C10-C36)
Diesel Fuel #2	2.0 mL	Acetone	46 mL	50 mL	2000 ug/mL	4000 µg/mL
Residual Range Calibration Standard	2.0 mL					

10.3.5. If kerosene, gasoline, fuel #6, mineral spirits or hydraulic fluid is requested to be reported by NwTPH-DX a minimum of a five point initial calibration is prepared and analyzed at the levels indicated in the table below. The baseline window is determined by setting the integration parameters to encompass the majority of the baseline rise in the highest level of the calibration. Use this window to integrate all of the calibration levels. This window can be verified with the CCV daily and adjusted if maintenance is performed that would shift the window slightly (clipping small amounts of column for example).

Concentration (µg/mL)						
Compound	**Std 1**	**Std 2**	**Std 3**	**Std 4**	**Std 5**	**Std 6**
Kerosene	125	250	500	1000	2500	5000
Mineral Spirits	125	250	500	1000	2500	5000
Hydraulic Fluid	-	250	500	1000	2500	5000
Diesel Fuel #6	-	250	500	1000	2500	5000
Heavy Fuel Oil Range	-	250	500	1000	2500	5000

11. Calibration and Standardization

11.1. Table 11.1 Calibration and Standardization.

Calibration Metric	Parameter / Frequency	Criteria	Comments
Balance Calibration	Daily before use	See Support Equipment SOP S-MN-Q-264	See Support Equipment SOP S-MN-Q-264
Retention Time Marker	Ran once per day prior to first opening CCV or ICAL		See Table 13.1
	AK102 – C10 and C25	0.1 min prior to C10 and ending at 0.1 min prior to C25	Retention times on a MACH/LTM system are set to .05 min prior to (or after) each carbon peak.
	AK103 – C25 and C36	0.1 min prior to C25 and ending at 0.1 min after C36	
	8015 Diesel Range Organics	0.1 min prior to C10 and ending at 0.1 min after C28	
	8015 C10-C36	0.1 min prior to C10 and ending at 0.1 min after C36	
	8015 Motor Oil Range Organics	0.1 min prior to C24 and ending at 0.1 min after C36	
	NwTPH DRO	0.1 min prior to C12 and ending at 0.1 min after C24	
	NwTPH ORO	0.1 min after C24 to 0.1 min after C40	
	Surrogates	RT times are assigned when each surrogate is integrated manually.	
Calibration Curve Fit (AK 102/103)	Average Response Linear Regression Non-linear Regression	25% RSD $r \geq 0.995$ $COD \geq 0.995$	If not met, try non-linear regression fit. If still not met, remake standards and recalibrate and verify before sample analysis.
Calibration Curve Fit (NwTPH)	Average Response Linear Regression Non-linear Regression	<15% RSD $r \geq 0.99$ $COD \geq 0.99$	If not met, try non-linear regression fit. If still not met, remake standards and recalibrate and verify before sample analysis.

Calibration Curve Fit (8015)	Average Response Linear Regression Non-linear Regression	<20% RSD r ≥ 0.99 COD ≥ 0.99	If not met, try non-linear regression fit. If still not met, remake standards and recalibrate and verify before sample analysis.
Second Source Verification Standard (ICV)	Immediately after each initial calibration	AK 102/103 % Diff ±25% NwTPH % Diff ±15% 8015 B % Diff ±15% 8015 C/D % Diff ±20% Unless other criterion is specified by a client QAPP or Tech Specs an additional ±10% is allowed for an ICV.	If the requirements for initial calibration are not met, review standard preparation. Evaluate the instrument for any errors. Only two injections of the same standard are permitted back to back If the second analysis does not meet criteria, recalibrate the instrument prior to sample analysis. A solvent rinse should be run after level 10, prior to ICV, to remove carry-over.
Continuing Calibration Verification (CCV)	Prior to the analysis of any samples at the beginning of each analytical shift not to exceed 24 hours, suggested to bracket each batch of QC and 20 samples. 8015 requires a CCV every 10 injections	AK 102/103 % Diff ±25% NwTPH % Diff ±15% 8015 B % Diff ±15% 8015 C/D % Diff ±20%	If the requirements for continuing calibration are not met, review standard preparation. Evaluate the instrument for any errors. Only two injections of the same standard are permitted back to back If the second analysis does not meet criteria, recalibrate the instrument prior to sample analysis.
Blank (solvent or method blank)	Following the first daily CCV	Target analytes must be less than reporting limit. If results are reported to MDL, target analytes in MB should be non-detect.	Evaluate to determine the cause of the contamination. Reanalyze. Perform and necessary instrument maintenance. Re-analyze associated samples.
Reporting Limit Verification	Requant the reporting limit standard in the ICAL against the ICAL after initial ICAL and every 30 days then, after the life of the ICAL.	60-140%	If the criterion is not met, evaluate the data quality objectives of the samples to be analyzed, if the next standard meets the criteria and DQO, raise the reporting limit. If the lowest calibration standard is required to meet the RL DQO, recalibrate the instrument prior to sample analysis.

12. Procedure

12.1. Aqueous Sample Preparation

12.1.1. Allow the samples to warm to room temperature. Measure the pH of the sample by pipetting a small amount of sample using a Pasteur pipette onto a pH strip. Record the pH on the extraction sheet. Measure the sample volume by marking the meniscus of the sample volume on the container. Pour the sample into a 2L pre-rinsed separatory funnel labeled with the corresponding sample identification number. Determine the volume of the sample volume received by filling the sample container with water to the marked meniscus line and measuring the volume using a class A graduated cylinder.

12.1.2. Prepare a method blank by pouring 250 mL for AK102, AK 103 and NwTPH and 500mL for 8015 of deionized water into a 2L separatory funnel and preserving to the same pH as the sample aliquots with 1:1 HCl approximately 0.5 mL of 1:1 HCl for 250 mL and 1 mL for 500 mL.

12.1.3. Prepare a laboratory control sample and laboratory control sample duplicate (LCS/LCSD) by measuring 250 mL for AK102, AK 103 and NwTPH and 500mL for 8015 of deionized water into a 2L separatory funnel and preserving to the same pH as the sample aliquots with 1:1 HCl approximately 0.5 mL of 1:1 HCl for 250 mL and 1 mL for 500 mL.

12.1.4. A matrix spike (MS) and matrix spike duplicate (MSD) are prepared by measuring two additional 250 mL aliquots for AK102, AK103 and NwTPH and 500 mL aliquots for 8015 of a designated environmental sample into two separate separatory funnels. If insufficient sample is available to prepare MS/MSD, an LCS/LCSD set must be prepared with the extraction batch.

12.1.4.1. The state of WI requires a set of MS/MSD in a batch if the sample is from WI. If there is insufficient sample for a MS/MSD the extra container from the state of WI must be split into 3 portions (parent, MS and MSD). A placeholder must be requested from the PM and used as the parent sample. The volume will then be brought up for extraction purposes.

12.1.5. For NwTPH batches 1 sample dup is required per every 10 samples. An MS/MSD can count as one dup.

12.1.6. Spike the sample aliquots, LCS/LCSD, and/or MS/MSD with 250 uL of matrix spike. Spike all samples with 25 uL of o-terphenyl and 10 uL of n-triacontane d62.

12.1.7. Add 15 mL of Methylene Chloride for AK 102, AK 103 and NwTPH and 30 mL of Methylene Chloride for 8015 to the sample and MS/MSD containers, or directly to the separatory funnels for method blank and LCS. Rinse the containers and add the solvent to the sample separatory funnel. Shake each separatory funnel for 4 minutes on the automatic shaker with periodic venting to release excess pressure.

NOTE: Methylene Chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Venting of the separatory funnels should be into a hood to avoid needless exposure of the analyst to solvent vapors.

12.1.8. Allow the organic layer to separate from the water phase.

12.1.9. Drain the Methylene Chloride layer (bottom layer) into a pre-rinsed sodium sulfate funnel and flask.

12.1.10. Repeat steps 12.1.6 through 12.1.8 two more times using fresh 15 mL portions of Methylene Chloride for AK 102, AK 103 and NwTPH and fresh 30 mL portions of Methylene Chloride for 8015, collecting and combining the solvent layer in same Erlenmeyer flask. Only the initial aliquot has to be used to rinse the sample container.

12.1.11. For sample extraction preparation, see section 12.3.

12.2. Soil Sample Preparation – Sonication

12.2.1. Allow the samples to come to room temperature. The sample should be homogenized by stirring the sample with stainless steel spatula. Weigh out 10 grams of each sample to the nearest 0.1 g into a tared 400 mL beaker labeled with the sample identification number. Record on the extraction sheet the weight of each sample to the nearest 0.1g.

12.2.2. Prepare a method blank and laboratory control samples by weighing out three 10 gram aliquots of reagent free sand into three separate beakers.

12.2.3. A matrix spike and matrix spike duplicate are prepared by weighing two 10g aliquots aliquots of a designated environmental sample into two separate 400 mL beakers. If there is insufficient sample available to prepare MS/MSD, an LCS/LCSD set must be prepared with the extraction batch. For NwTPH batches 1 sample dup is required per every 10 samples. An MS/MSD can count as one dup.

12.2.4. Each method blank, LCS/LCSD and MS/MSD is labeled by the extraction batch identification from the LIMS.

12.2.5. Add anhydrous sodium sulfate to each beaker. Mix well with a stainless steel utensil. If required, more sodium sulfate may be added. After addition of the sodium sulfate, the sample should be free flowing.

12.2.6. Spike the sample aliquots, LCS/LCSD, and/or MS/MSD with 25 uL of o-terphenyl and 10 uL of n-triacontane d62. Then spike the LCS/LCSD and or MS/MSD with 500 uL of matrix spike.

12.2.7. Immediately add 60 mL of 80:20 $MeCl_2$:acetone to each beaker.

12.2.8. Clean the sonicator probe by washing with Methylene Chloride and wipe with a disposable tissue.

12.2.9. Tune the sonicator following procedures outlined in the sonication SOP S-MN-O-414, or equivalent replacement.

12.2.10. Place the sample in the sonicator.

12.2.11. Lift the probe.

12.2.12. Place sample in the middle of the platform.

12.2.13. Lower probe in the beaker. Place the tip of the disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer. The platform may be adjusted by turning the labjack.

12.2.14. Close the door and latch.

12.2.15. Turn the sonicator on.

- Direction will appear on the screen.
- Press ‘prog’, the sonicator should be set to pulse for 1.5 minutes at 1.5 pulses/second.
- Press ‘start’.

12.2.16. When pulsing stops, remove the sample. Rinse the probe with Methylene Chloride into the sample.

12.2.17. Carefully decant solvent into funnel with fluted filter paper. The soil should remain in the beaker until the final sonication is complete.

12.2.18. Repeat the procedure of adding solvent, sonicating and filtering two more times using fresh portions of Methylene Chloride.

12.2.19. After the third ultrasonic extraction, pour the entire sample into the fluted filter paper funnel and rinse with Methylene Chloride.

- Use a stainless steel utensil to push the soil into the funnel if needed. Rinse the beaker and stainless steel utensil with Methylene Chloride into the funnel OR
- Use a wash bottle and a minimal amount of Methylene Chloride to wash the soil into the funnel.

12.2.20. Continue filtration until all visible solvent is removed from the funnel.

12.3. Extract Preparation

12.3.1. Perform the concentration using the Kuderna-Danish (K-D) Technique. Assemble a prerinsed K-D apparatus by attaching a 10 mL concentrator tube to a 500 mL K-D flask with a clamp. Add one boiling chip to each apparatus.

12.3.2. Each sample is dried using prebaked granular sodium sulfate. A minimal amount of sodium sulfate is added to the extract and swirled vigorously. The sample is decanted into a 500mL assembled K-D apparatus and the sodium sulfate is rinsed with Methylene Chloride and quantitatively transferred to the KD.

12.3.2.1. Taking the graduated concentrator tube and joining it to the 500 mL Kuderna Danish assembles the K-D apparatus.

12.3.2.2. A blue clamp is used to ensure the two pieces of glassware do not come apart on the waterbath.

12.3.3. Attach a three-ball macro Snyder column to the top of the K-D flask. Place the K-D apparatus on a hot water bath so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in steam vapors. At the proper rate of distillation the ball of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 4-6 mLs, remove the K-D apparatus from the bath, remove the clamp connecting the concentrator tube and K-D flask, and allow it to drain and cool. DO NOT allow the extract to go to dryness.

12.3.4. Remove the 3-ball macro Snyder column from the K-D flask. Set aside to be cleaned and allow to cool.

12.3.5. Use nitrogen to evaporate the extract in the concentrator tube to 1.0 mL. DO NOT allow the extract to evaporate to dryness. Ensure that the nitrogen stream does not bubble, but only an indentation is apparent on the surface on the extract. Bring the extract to a final volume (1.0 mL) in a disposable serological pipette. Using Methylene Chloride, bring the extract up in a pipette so that the bottom of the meniscus is at the 1 mL mark. Place the 1 mL into an autosampler vial labeled with the sample identification number. Crimp cap the vial and store at less than -10 ºC for AK102/103 and <6 ºC but above freezing for 8015 and NwTPH. The extracts are ready for analysis.

12.4. Optional Sample Clean-up – if requested by the client

12.4.1. For NwTPH if the client requests Silica Gel cleanup:

12.4.1.1 The extract may be brought up to 10 mL for clean-up purposes and transferred to a capped 20 mL vial. Add ~ 0.4 grams of silica gel, cap and mix by hand shaking for 10 seconds. Repeat the silica step one additional time.

12.4.1.2 You may utilize smaller aliquots or volumes of the extract for this process as long as you keep the ratios approximately the same.

12.4.1.3 Prepare a stainless steel funnel with glass wool (methylene chloride rinse the funnel with wool) and pour the sample though to remove the silica. Place the 20 mL vial with the sample on the N-Evap and concentrate down to a final volume of 1 mL.

12.4.2. For AK 102/103 and 8015 if the client requests Silica Gel cleanup after initial run by micro silica column:

12.4.2.1 The cleanup procedure typically takes place after the initial AK or 8015 extract has been analyzed and client evaluates the results. It is important that the original extract be used to minimize the variability of non-homogeneous samples.

12.4.2.2 The micro column is created by filling a 5 ¾ inch Pasteur pipet ¾ full with silica gel. The column is then placed into a 1 liter jar containing Methelyne Chloride

and allowed to soak. Do not use the silica columns until the silica gel has been fully saturated with methylene chloride. Once saturated place the columns in the metal column holder stand located in O-prep.

12.4.2.3 Uncap the vials containing the sample and transfer the extract to the top of the column with a disposable pipet. Rinse the extract vial with 1 mL of MeCl and transfer to the top of the column. Repeat 3 times.

12.4.2.4 Elute with additional MeCl to obtain a total of 7 mL of solvent collected into a 7mL vial.

12.4.2.5 Concentrate down to a final volume of 1 mL on the N-Evap.

12.5. Sample Analysis

12.5.1. Inject an aliquot (typically 1-3µL) of sample extract on the column. Example GC operating conditions are listed in Table 1 but may be changed to optimize method efficiency.

12.5.2. Samples are quantified by dividing the total area response by the average response factor. Baselines are drawn from the lowest point in the chromatogram following the general pattern that Methylene Chloride solvent blanks exhibit. The average response factor derived from the current initial calibration curve is used to quantitate each sample.

12.5.3. If the response for the peaks of interest in the sample exceeds the working range of the calibration curve, the extract will be diluted and reanalyzed so that it is within the upper calibration range when possible. Dilutions shall be performed within holding time.

12.5.4. The area of the surrogate is subtracted from the total Diesel Range Organic area.

12.5.5. Samples following high standards or over-range samples are to be monitored for carryover.

13. Quality Control

13.1. Table 13.1 Quality Control, Criteria and Corrective Action.

QC Sample	Components	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	Reagent water or Baked and rinsed sand per SOP S-MN-O-500	One per 20 samples	Target analytes must be less than reporting limit. If results are reported to MDL, target analytes in MB should be non-detect	Re-analyze associated samples. ***Exceptions:*** If sample ND, report sample without qualification; If sample result >10x MB detects, report sample as not impacted by the blank contamination; If sample result <10x MB detects and sample cannot be reanalyzed, report sample with appropriate qualifier to indicate an estimated value. Client must be alerted and authorize this condition. For WI samples, evaluate the MB to the MDL. If detections are present between the MDL and RL, qualify appropriately. For detections above the RL, data is acceptable to report only if sample concentrations are 10x greater, otherwise re-prep and re-analyze.

Laboratory Control Sample (LCS)/ Laboratory Control Sample Duplicate (LCSD - required for AK 102/103)	DI water or Baked and rinsed sand per SOP S-MN-O-500 spiked with all target compounds	One per 20 samples	AK102 – 75-125% AK103 – 60-120% %Diff $\leq$ 20% NwTPH-Dx – 50-150% 8015 – internally generated limits	Reanalyze the LCS; If problem persists, check spike solution; Perform system maintenance prior to further analysis. If biased low, re-extract the entire batch accordingly if sufficient volume remains. ***Exceptions:*** If LCS recovery is > QC limits and these compounds are non-detect in the associated samples, the sample data may be reported with appropriate data qualifiers.
Matrix Spike (MS)	Client sample spiked with all target compounds	One per 20 samples	AK102, AK103, NwTPH-Dx – 50-150% 8015 – internally generated	If there is an outlier, the corresponding laboratory control spikes must be evaluated. If the same outlier occurs in the LCS, a system problem may be assumed. In this instance, samples may have to be reanalyzed. If the LCS reports an acceptable recovery, matrix interferences are assumed. In either instance, the data on the final report must be footnoted with the outliers and possible reason if known.
MSD / Duplicate	MS Duplicate *OR (alternative)* Sample Dup	One for every 20 of samples For NwTPH the method requires 1 sample duplicate for every 10 samples. An MS/MSD can count as one Duplicate.	%Diff $\leq$ 30%	Report results with an appropriate footnote. Flag the same as if the LCS is bias high. For Minnesota Admin Contract clients – all MS/MSD failures require reanalysis of the MS/MSD and the original sample. If it is still out of control, investigated and document the cause in the associated narrative as well as qualifying appropriately.
Surrogate	Labeled standard added to all standards, quality control samples and samples	In every analytical run	AK102 and AK103: 60-120% for QC and 50-150% for samples NwTPH-Dx – 50-150% 8015 – internally generated	Recoveries outside of acceptance limits with no visible matrix interferences should be re-run at a minimum to confirm. If re-analysis yields similar results, the sample should be re-extracted if there is sufficient sample or the client may be contacted to inquire about further action (some clients may need results ASAP for rush requests.) Surrogates biased high with no detectable results may be reported as the high bias is deemed to have no impact.

14. Data Analysis and Calculations

14.1. Percent Difference for CCV**:**

$$Percent\ Difference = \left| \frac{C_{nom} - C_{calc}}{C_{nom}} \right| x100$$

where:

C_{nom}	=	True value of the continuing calibration standard
C_{calc}	=	Calculated value of the continuing calibration standard

14.2. The chromatogram report will contain the extract concentration or "On-Column" amount, in ug/mL. This value will be converted to sample concentration in mg/L for water and mg/kg for soil using the equations below:

Concentration, Aqueous

$$Conc(mg/L) = \frac{(V_t)(D)}{(V_i)(V_s)}$$

Concentration, Soil

$$Conc(mg/kg) = \frac{(V_t)(D)}{(V_i)(W)}$$

where:

V_i	=	Volume of extract injected
D	=	Dilution factor. If no dilution D=1
V_t	=	Volume of total extract, mL.
V_s	=	Volume of water extracted, mL
W	=	Dry weight of sample extracted, g

14.3. The following calculation can be used to calculate the LCS and MS percent recovery (where SampleConc would be equal to 0 for LCS):

$$\%REC = \frac{(MSConc - SampleConc)}{TrueValue} * 100$$

14.4. The relative percent difference (RPD) between the recoveries in the LCS/LCSD and MS/MSD will be calculated and reported using the following equation:

Relative Percent Difference

$$RPD = \frac{|LCSR - LCSDR|}{(LCSR = LCSDR)/2} x100$$

$$RPD = \frac{|MSR - MSDR|}{(MSR + MSDR)/2} x100$$

where:

LCSR/LCSDR	=	LCS/LCSD % Recovery
MSR/MSDR	=	Matrix Spike/Matrix Spike Duplicate %recovery

14.5. The following equation is used to calculate percent recovery of pentacosane:

Surrogate Percent Recovery

$$\%\ Recovery = \frac{C_x}{C_{SA}}$$

where:

C_x = concentration of analyte measured in sample

C_{SA} = concentration of analyte added to sample

14.6. The following equation is used to calculate the relative standard deviation (RSD):

$$RSD = \frac{S}{\overline{X}} \times 100$$

where:

S = Standard Deviation of the data points

$\overline{X}$ = Average of all data points

15. Data Assessment and Acceptance Criteria for Quality Control Measures

15.1. See tables in section 11 & 13.

16. Corrective Actions for Out-of-Control Data

16.1. See tables in section 11 & 13.

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

17.1. If not specifically listed in the tables in section 11 & 13, the contingencies are as follows. If there is no additional sample volume to perform re-analyses, all data will be reported as final with applicable qualifiers. If necessary, an official case narrative will be prepared by the Quality Manager or Project Manager.

18. Method Performance

18.1. All applicable personnel must read and understand this SOP with documentation of SOP review maintained in their training files.

18.2. **Method Detection Limit (MDL) Study**: An MDL study must be conducted annually (per the method) per S-MN-Q-269, Method Detection Limit Studies for each matrix per instrument.

18.3. **Demonstration of Capability (DOC)**: Every analyst who performs this method must first document acceptable accuracy and precision by passing a demonstration of capability study (DOC) per S-MN-Q-279, Training and Employee Orientation.

18.4. **Periodic performance evaluation (PE)** samples are analyzed to demonstrate continuing competence per SOP S-MN-Q-258 (or equivalent replacement). Results are stored in the QA office**.**

19. Method Modifications

19.1. The silica gel cleanup method for AK102/103 is modified from the method. The method states to use 10 mL pipettes and Pace uses 2 mL Pasteur pipettes.
19.2. For Method 8015B/C/D, this is an expansion of the method to report the oil range organics component in order to measure petroleum products that elute in the carbon range from the beginning of C24 to the end of C36. Retention time windows and method performance are monitored for this expansion. A total C10-C36 range may be reported referencing this method for client specific data quality objectives.
19.3. AK methods only require MeCl2 for extraction but 80:20 MeCl2:Acetone mix is used in place.

20. Instrument/Equipment Maintenance

20.1. Please refer to the GC instrument manual for maintenance procedures performed by the lab.

20.2. All maintenance activities are listed daily in maintenance logs that are assigned to each separate instrument.

21. Troubleshooting

21.1. If calibrations are failing and injection port maintenance and or a new column fails to bring the system back into calibration it is likely that the FID jet and or the FID detector nut ferrule may need to be replaced.

22. Safety

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

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

23. Waste Management

23.1. Procedures for handling waste generated during this analysis are addressed in *S-MN-S-003 - Waste Handling*.

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

24. Pollution Prevention

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

25. References

25.1. Pace Quality Assurance Manual- most current version.

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

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

25.4. Method AK 102, Determination of Diesel Range Organics, Alaska Department of Ecology, Version 04/08/02.

25.5. Method AK 103, Determination of Residual Range Organics, Alaska Department of Ecology, Version 04/08/02.

25.6. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Online, December 1996, Revision 2, Method 8000B-96.

25.7. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Online, March 2003, Revision 3, Method 8000C-03.

25.8. Analytical Methods for Petroleum Hydrocarbons; NWTPH-Dx, June 1997, ECY 97-602

25.9. Method 8015C, Nonhalogenated Organics by Gas Chromatography

25.10. Method 8015D, Nonhalogenated Organics Using GC/FID

26. Tables, Diagrams, Flowcharts, and Validation Data

26.1. Table I: Chromatographic Conditions

26.2. Attachment I: Ranges AK/8015/Nw Definition

26.3. Attachment II: Water Extraction Sheet

26.4. Attachment III: Water Extraction Sheet with Silica Gel Clean Up

26.5. Attachment IV: Soil Sonication Extraction Sheet

27. Revisions

Document Number	Reason for Change	Date
S-MN-O-578-Rev.07	Added "/D" to Reference Method on cover page, header, 1.1, and 19.2 for 8015. Table 11.1 – Criteria for ICV and CCV rows – added "/D" to 8015. Added References 25.9 and 25.10. Table I – updated all specifications.	09Jul2018
S-MN-O-578-Rev.08	Table 7.1 – Hold Time for Aqueous sample type updated with separate hold time for 8015, added "8015 hold time is 7 days for preserved and unpreserved samples." 10.3.5 – corrected typo for Hydraulic Fluid Std 6 to 5000, was incorrectly 500	24Jul2018

Table I: Chromatographic Conditions

Gas Chromatograph: Agilent 7890A, equipped with an Agilent G2614A autosampler interfaced to a Target data system (or equivalent).

Column Conditions: LTM DB-5 (or equiv) 10m x 0.32mm x 0.5um

Injection Port: Injection temperature = 300°C, sample injection volume = 2 µL, splitless injection. Constant Pressure at 10 PSI

Oven Temperature Program: Constant at 280°C.

Detector: Flame Ionization Detection (FID) - Detector temperature 320°C

Attachment I: Ranges AK/8015/Nw Definition

Pace Analytical®	Document Name: Ranges AK/8015/Nw	Document Revised: 07August2015 Page 1 of 1
	Document No.: F-MN-O-254-rev.02	Issuing Authority: Pace Minnesota Quality Office

Ranges AK/8015/Nw

DRO by AK102	C10 – C25* (before)
RRO AK103	C25* (before) – C36
TPH-DRO (C10-C28) [8015]	C10 – C28
Motor Oil Range (C24-C36) [8015]	C24 – C36
C10-C36 [8015]	C10 – C36
Diesel Fuel Range [NwTPH]	C12 – C24* (after)
Diesel Fuel Range SG [NwTPH silica]	C12 – C24* (after)
Motor Oil Range [NwTPH]	C24* (after) – C40
Motor Oil Range SG [NwTPH silica]	C24* (after) – C40

*no overlap, example: AK102 C-25 begins 7.00 then AK103 C-25 begins at 7.01

Attachment II: Water Extraction Sheet

Pace Analytical	Document Name: Extraction Method: SW 3510 Separatory Funnel Extraction Analysis: AK102/AK103, 8015B/C, NwTPH-Dx – Water	Document Revised: 07May2014 Page 1 of 1
	Document No.: F-MN-O-251-rev.07	Issuing Authority: Pace Minnesota Quality Office

☐ AK102/AK103 ☐ 8015B/C ☐ NwTPH-Dx

SS (1):		Amt:	25 µL	Analyst:	Ext. Date/By:
SS (2):		Amt:	10 µL	Analyst:	Batch:
MS:		Amt:	250 µL	Analyst:	Dispensor/Syringe IDs:

SS (1): o-terphenyl: 2,000 µg/mL SS (2): n-triacontane d62: 5,000 µg/mL MS: Diesel/MO: 2,000 µg/mL

	Sample ID	500 mL (8015B/C) 250 mL (AK102/AK103, NwTPH) IV	pH	Spike Ver.	F.V. 1.0 mL (clear) Lot #	Comments
1	MB-					
2	LCS-					
3	LCSD-					
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						

Sample IDs Verified:		1:1 HCl:		Bath Temp Read (80°C):	°C
Na_2SO_4:		Silica Lot:		Bath Temp Corrected:	°C
		Glass Wool Lot:		Thermometer ID:	
MeCl2:		Date Conc./By		Pipettor ID:	

Comments:

Posted by:	Date:	Validated by:	Date:

Attachment III: Water Extraction Sheet with Silica Gel Clean up

Pace Analytical	Document Name: Extraction Method: SW 3510 Separatory Funnel Extraction Analysis: AK102/AK103, 8015B/C, NwTPH-Dx – Water (with Silica Gel Clean Up)	Document Revised: 07May2014 Page 1 of 1
	Document No.: F-MN-O-252-rev.06	Issuing Authority: Pace Minnesota Quality Office

☐ AK102/AK103 ☐ 8015B/C ☐ NwTPH-Dx

SS (1):		Amt: 25 µL	Analyst:	Ext. Date/By:	
SS (2):		Amt: 10 µL	Analyst:	Batch:	
MS:		Amt: 250 µL	Analyst:	Dispensor/Syringe IDs:	

SS (1): o-terphenyl: 2,000 µg/mL SS (2): n-triacontane d62: 5,000 µg/mL MS: Diesel/MO: 2,000 µg/mL

	Sample ID	500 mL (8015B/C) 250 mL (AK102/AK103, NwTPH) IV	pH	Spike Ver.	Date Conc. (MeCl2)	F.V. 1.0 mL (clear) Lot #	Comments
1	MB-						
2	LCS-						
3	LCSD-						
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							
25							

Sample IDs Verified:		1:1 HCl:		Bath Temp Read (80°C):	°C
Na_2SO_4:		Silica Lot:		Bath Temp Corrected:	°C
		Glass		Thermometer ID:	
MeCl2:		Wool Lot:		Pipettor ID:	

Comments:

Posted by:	Date:	Validated by:	Date:

Attachment IV: Soil Sonication Extraction Sheet

Pace Analytical	Document Name: Extraction Method: SW 3550 MicrowaveAnalysis: AK102/AK103, 8015, NwTPH-Dx – Soil	Document Revised: 25Sep15 Page 1 of 1
	Document No.: F-MN-O-253-rev.05	Issuing Authority: Pace Minnesota Quality Office

☐ AK102/AK103 ☐ 8015 ☐ NwTPH-Dx

SS (1):		Amt:	25 µL	Analyst:	Ext. Date/By:
SS (2):		Amt:	10 µL	Analyst:	Batch:
MS:		Amt:	250 µL	Analyst:	Dispensor/Syringe IDs:

SS (1): o-terphenyl: 2,000 µg/mL SS (2): n-triacontane d62: 5,000 µg/mL MS: Diesel/MO: 2,000 µg/mL

	Sample ID	10 grams IV	Spike Ver.	F.V. 1.0 mL (clear) Lot #	Comments
1	MB-	10			Sand Lot #:
2	LCS-	10			Sand Lot #:
3	LCSD-	10			Sand Lot #:
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					

Sample IDs Verified:	Na_2SO_4:	Silica Lot:
$MeCl_2$/Acetone:	Date Conc./By:	$MeCl_2$ Final Volume /Pipet:
Microwave ID:	Buchi ID:	Filter Paper Lot #:
Comments:		
Posted By: Date:	Validated by:	Date:

ALS Standard Operating Procedure

DOCUMENT TITLE:	DETERMINATION OF HYDROGEN, CARBON MONOXIDE, CARBON DIOXIDE, NITROGEN, METHANE, AND OXYGEN USING GAS CHROMATOGRAPHY WITH THERMAL CONDUCTIVITY DETECTION (TCD) IN ACCORDANCE WITH EPA METHOD 3C OR ASTM D 1946
REFERENCED METHOD:	EPA METHOD 3C, ASTM D 1946
SOP ID:	VOA-EPA3C
REV. NUMBER:	14.0
EFFECTIVE DATE:	12/31/2016

STANDARD OPERATING PROCEDURE

DETERMINATION OF HYDROGEN, CARBON MONOXIDE, CARBON DIOXIDE, NITROGEN, METHANE, AND OXYGEN USING GAS CHROMATOGRAPHY WITH THERMAL CONDUCTIVITY DETECTION (TCD) IN ACCORDANCE WITH EPA METHOD 3C OR ASTM D 1946

EPA METHOD 3C, ASTM D 1946

SOP ID:	VOA-EPA3C	Rev. Number:	14.0	Effective Date:	12/31/2016

Approved By: _____ Date: 12/15/16
Volatiles GC Team Leader - Mike Conejo

Approved By: _____ Date: 12/14/16
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Approved By: _____ Date: 12/14/16
QA Manager - Chaney Humphrey

Approved By: _____ Date: 12/14/16
Laboratory Director - Kelly Horiuchi

Archival Date:	_____	Doc Control ID#:	Uncontrolled	Editor:	_____

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DETERMINATION OF HYDROGEN, CARBON MONOXIDE, CARBON DIOXIDE, NITROGEN, METHANE, AND OXYGEN USING GAS CHROMATOGRAPHY WITH THERMAL CONDUCTIVITY DETECTION (TCD) IN ACCORDANCE WITH EPA METHOD 3C OR ASTM D 1946

1) Scope and Applicability

1.1 The referenced method (EPA Method 3C) was written for the analysis of carbon dioxide, methane, nitrogen and oxygen, in municipal solid-waste landfill gas and other stationary sources but is easily modified for the gas chromatographic method determination of hydrogen and carbon monoxide. In contrast, the practice ASTM D 1946 covers the determination of the chemical composition of reformed gases and similar gaseous mixtures containing each of these six components. Method ASTM D 1945-03 modified which describes the analysis of natural gas may also be referenced.

1.2 This method is appropriate for quantifying target analyte gases depending on the concentration of the samples from approximately 500 ppmv to high percent values. The number of samples, which may be analyzed in one eight hour day, is approximately twenty. The reporting limits for these analytes are listed in Attachment 4 of this standard operating procedure.

2) Summary of Procedure

2.1 The EPA Method 3C was written for use with backfilled summa canisters but is easily modified for samples collected as vapor in Tedlar bags, steel tanks, glass bottles, summa or other specially prepared canisters. In contrast, the ASTM methods do not specify a requirement for the sampling container.

2.2 An aliquot is drawn from the sampling container using a sample loop and injected onto a packed chromatographic column where the analytes are separated and measured using a thermal conductivity detector (TCD). Samples are analyzed in duplicate for EPA Method 3C, but a modification may be made which entails a single injection per submitted field sample. However, results from samples analyzed per ASTM D 1946 are obtained using a single injection technique.

Note: Refer to Sections 12.13 and 15.9 for the list of reporting modifications for these methods.

3) Definitions

3.1 Analytical Sequence The analytical sequence describes exactly how the field and QC samples in an analytical batch are to be analyzed.

3.2 Field Sample A sample collected and delivered to the laboratory for analysis.

3.3 Batch QC The QC samples that are analyzed in an analytical batch of field samples and includes the Method Blank (MB), Laboratory Control Sample (LCS) or Laboratory Duplicate (LD).

3.4 Calibration Standard (Initial Calibration – ICAL) A calibration standard of a known concentration containing desired analyte(s) prepared from a primary standard, which is, in turn, prepared from a stock standard material. A calibration standard is injected at varying volumes and used to calibrate the response of the measurement system with respect to analyte concentration.

3.5 Initial Calibration Verification (ICV) Standard An ICV is a standard that is obtained from a source other than the source for the calibration standards and is analyzed after the

measurement system is calibrated, but prior to sample analysis in order to verify the initial calibration of the measurement system.

3.6 Method Blank (MB) An analyte-free matrix, which is carried through the entire analytical process. It is used to evaluate the process for contamination from the laboratory.

3.7 Laboratory Control Sample (LCS) An LCS is a standard that is obtained from a source other than the source for the continuing calibration verification standard (CCV). The percent recovery of the analyte(s) in the LCS is used to assess method performance.

3.8 External Standard Calibration External standard calibration involves comparison of instrument responses from the sample to the responses from the target compounds in the calibration standards. Sample peak areas or peak heights are compared to peak areas or peak heights of the standards.

3.9 Analytical Batch A group of samples which behave similarly with respect to the sampling or the test procedures being employed and are processed as a unit using the sample lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. In an analytical batch of samples, the time period is 24 hours or up to twenty sample injections, whichever comes first of continuous operation without interruption.

3.10 Continuing Calibration Verification (CCV) Standard A continuing calibration verification standard is a midrange calibration standard that is analyzed periodically to verify the continuing calibration of the measurement system.

3.11 Precision Precision of a method is how close results are to one another, and is usually expressed by measures such as standard deviation, which describe the spread of results.

3.12 Bias The bias of a method is an expression of how close the mean of a set of results (produced by the method) is to the true value.

3.13 Manual Integration This term applies to a data file in which setpoints have been changed and reintegration has occurred under the changed setpoints; baselines have been adjusted; peak integration start and stop “ticks” have been changed; peak area, or peak height, are changed after the time of data collection and data file generation.

3.14 Ambient Air Ambient air within the laboratory which is sampled and analyzed once per batch to assess injector performance.

3.15 Limit of Detection (LOD) The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%. (DoD Clarification). For consistency purposes, the LOD may be referred to as the MDL once it is reported; however, full verification will be on file in the laboratory per the procedures detailed in this document.

3.16 Limit of Quantitation (LOQ) The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. (DoD Clarification). For consistency purposes and since the LOQ and MRL are equivalent with regards to laboratory procedure, the LOQ will be referred to as the MRL in this document and once it is reported. Full verification will be on file in the laboratory per the procedures detailed in the document.

3.17 Detection Limit (DL) / Method Detection Limit (MDL) The smallest analyte concentration that can be demonstrated to be different from zero or a blank concentration at the 99% level of confidence. At the DL, the false positive rate (Type 1 error) is 1%. (DoD Clarification). For consistency purposes, the DL may be referred to as MDL. Also, as far as reporting is concerned the MDL will be raised (where necessary) to the verified LOD per the procedures defined in this document and reported accordingly.

4) Health and Safety Warnings

4.1 Each compound, mixture of compounds, standards, as well as samples, should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest level possible through the use of hoods (to minimize inhalation). For proper handling, use, and disposal refer to the laboratory's *Environmental Health and Safety Manual*, Safety Data Sheets (located in the safety cubicle in the front office), as well as the *SOP for Waste Disposal*.

4.2 Safety Data Sheets (SDS) Safety Data Sheets (SDS) are available in the Safety cubicle located in the front office and shall be reviewed as part of employee training.

4.3 Safety Glasses Safety glasses are required when performing maintenance on pressurized systems.

4.4 Pressurized Gases The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp at all times. The regulator should not remain on size "D" cylinders when not in use. Sources of flammable gases (i.e. pressurized hydrogen) should be clearly labeled.

4.5 Pollution Prevention and Waste Management All waste management must be carried out in accordance with the requirements detailed in the *SOP for Waste Disposal* as well as the *Environmental Health and Safety Manual*.

5) Cautions

5.1 A maintenance log shall be kept documenting maintenance performed on each analytical system and the instrument maintenance log must be kept current and reviewed quarterly. The serial numbers of each instrument shall be recorded in the front of the logbook. An entry must be made in the appropriate log each time any maintenance activity is performed (no matter the extent). The entry in the log must include:

(a) The date of maintenance
(b) Who did the maintenance
(c) Description of the maintenance
(d) Proof that the maintenance activity was successful

A notation of a successful continuing calibration or initial calibration shall serve as proof that the maintenance is complete and the instrument is in working order.

5.2 Carrier Gas Purifier If in-line purifiers or scrubbers are in place, these purifiers must be changed as recommended by the supplier.

5.3 GC System

5.3.1 Column Column performance should be monitored by observing peak shapes and column bleed. Over time, the column may exhibit a poor overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur depends on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be changed or the packing replaced (see Section 9.1.1). Care should be taken to minimize the introduction of air or oxygen into the column whenever GC maintenance is performed.

Decreasing performance can also be due to a leak in the system. Leaks can be detected with the use of a leak detector. Fittings may need to be tightened or ineffective column ferrules replaced to eliminate any leak detected.

5.3.2 Detector Replace filament assembly as needed.

5.3.3 Injection Lines Purge with nitrogen to ensure the line is not blocked.

6) Interferences

6.1 Contamination Dry ambient air at sea level contains 78.08% Nitrogen, 20.95% Oxygen, 0.93% Argon, and approximately 0.033% Carbon Dioxide by volume. Precautions must be taken to prevent intrusion of ambient air into the analytical system and the sampling containers.

6.1.1 Contamination in the Sample Care must be taken to prevent ambient air intrusion into the sample container during canister pressurization and laboratory analysis. When using adapters and fittings the dead volume should be evacuated and replaced with the sample gas prior to sampling from the container.

6.1.2 Carrier Gas Contamination To prevent system contamination, UHP/ZERO grade helium (99.999% purity) is used as the carrier gas. Also, a purifier and an oxygen trap are incorporated into the analytical system as additional insurance against possible contamination.

6.2 Peak Separation Since the TCD exhibits universal responses and detects all gas components except the carrier (helium, in this case), the appropriate temperature program, column flow rates and column packing must be used in order to separate all of the permanent gases with an exception of argon

6.3 Argon In this method, argon (0.93% by volume in ambient air) is not chromatographically separated from oxygen; therefore, results are reported as oxygen/argon.

7) Personnel Qualifications and Responsibilities

7.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review and reporting per the corresponding standard operating procedures. Laboratory personnel that have successfully demonstrated the ability to generate acceptable results according to this SOP are approved to perform sample analysis and interpretation of the results.

7.2 The department supervisor/manager or designee shall perform final review and sign-off on the data.

7.3 Demonstration of Capability

Training demonstrations shall be conducted in accordance with the *SOP for Training Policy,* DoD QSM, and TNI requirements. An initial demonstration of proficiency must be performed prior to independent analyses of samples. In addition, ongoing demonstration must be performed annually.

Once performance is found to be acceptable, a certification statement must be completed by the QA Manager and either the immediate supervisor or Laboratory Director and retained on file as a demonstration of compliance.

7.3.1 Quarterly Demonstration A demonstration of method sensitivity must be performed *quarterly on each instrument* performing this method.

1) A spike at the current LOD must be analyzed if results are to be reported below the MRL.
2) Verification of precision and bias at the LOQ must be performed.

Refer to Section 12.4 (LOQ) and 12.11.1 (LOD) for additional information on how these demonstrations are to be performed as well as the acceptance criteria.

7.3.2 Annual Demonstration Each analyst must perform this demonstration both initially and annually. Analyze four LCS standards at 1-4x the MRL (LOQ) either concurrently or over a period of days as a verification of precision and bias of the quantitation range. The standard deviation (n-1) and average percent recovery of the four replicates are compared against current laboratory control limits for precision and bias. See Attachment 4.

7.3.3 Change in Personnel, Instruments, Method and/or Matrix The requirements in Sections 7.3.1 and 7.3.2 must be performed per the schedule noted and when there is a change in personnel, instruments, method or matrix. "Change" refers to any change in personnel, instrument, test method, or sample matrix that potentially affects the precision and bias, sensitivity, or selectivity of the output (e.g., a change in the detector, column type, matrix, or other components of the sample analytical system, or a method revision).

All attempts at this demonstration must be completed and turned into the QA department for retention. Once performance is found to be acceptable, a required certification statement will be completed by the QA Manager and either the immediate supervisor or Laboratory Director and retained on file as a demonstration of compliance.

8) Sample Collection, Handling, and Preservation

8.1 The samples are collected and delivered to the laboratory for analysis in either Tedlar bags, specially prepared canisters, or glass sampling bottles (Bottle Vac. Entech Instruments). Samples collected in bags must be analyzed within 72 hours after sample collection unless otherwise specified by the client. Samples delivered in cleaned, evacuated summa or other specially prepared containers do not have a specified holding time for atmospheric gases but this laboratory recommends that samples be analyzed within 30 days from the date of collection.

9) Equipment and Supplies

9.1 Gas Chromatograph The analysis is performed using a Hewlett-Packard model 5890 series II gas chromatograph or equivalent equipped with a thermal conductivity detector.

9.1.1 Column 6' x 1/8" stainless steel column packed with 60/80-mesh carbosphere.

Conditioning of the chromatographic column is required prior to use of the system. The column should be conditioned with a continuous flow of chromatographic grade Helium and temperature programmed from 35˚C to 200˚C at a rate of five degrees per minute. The column should be held at 200˚C for at least four hours.

9.1.2 Sample Loop Stainless steel tubing with a 1/16" diameter (various lengths).

9.1.3 Conditioning System The system is able to maintain the column and sample loop at a constant temperature.

9.2 Adsorption Tubes In addition to a thermal gas purifier incorporated into the system, an oxygen trap shall be utilized to remove any O2 from the carrier gas to help in extending the life of the TCD filaments.

9.3 Sampling Media Tedlar bags, Summa canisters, or glass bottles may be supplied to the client for sampling purposes. These samples are submitted to the laboratory for analysis. Summa canisters must be conditioned and certified in accordance with the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters*.

10) Standards and Reagents

10.1 All samples, standards, and media must be stored separately. The concentration, preparation and expiration date as well as analyst's initials must be identified on the standard label. Each standard must also be uniquely identified with a laboratory ID number.

All standard certificates shall be noted with the standard identification number, date received and initials of the receiving analyst. They must then be given to the quality assurance department where they will be maintained. For additional information on these and other requirements, refer to the *SOP for Handling Consumable Materials.*

10.2 Carrier and Calibration Standard Balance Gas

10.2.1 Helium UHP/ZERO (99.999%) or higher in purity

10.3 Standards DoD compliance requires that second source standards be obtained from a second manufacturer or from a second lot obtained from the same manufacturer (independently prepared from different source materials).

10.3.1 Purchased Standards These standards must be stored in accordance with the requirements described in the *SOP for Handling Consumable Materials*. These standards must be stored at ambient temperatures for a period of up to 2 years or as recommended by the manufacturer.

10.3.1.1 Scott Specialty Gas or Equivalent

Compound	Concentration
Carbon dioxide	~5.00%
Carbon monoxide	~5.00%
Hydrogen	~4.00%
Methane	~4.00%
Nitrogen	~5.00%
Oxygen	~5.00%
Balance Gas: Helium	

Note: The concentrations of these standards will change with each purchase and the specific concentration of each compound will be denoted on the standard as well as the Certificate of Analysis and used in all calculations.

10.3.1.2 Matheson or Equivalent

Compound	Concentration
Carbon dioxide	~5.00%
Carbon monoxide	~5.00%
Hydrogen	~4.00%
Methane	~4.00%
Nitrogen	~5.00%
Oxygen	~5.00%
Balance Gas: Helium	

Note: The concentrations of these standards will change with each purchase and the specific concentration of each compound will be denoted on the standard as well as the Certificate of Analysis and used in all calculations.

10.3.1.3AirGas or equivalent (Neat gas standards)

Compound	Concentration
Hydrogen	99.999%
Carbon Monoxide	99.999%
Oxygen	99.999%
Nitrogen	99.999%
Methane	99.999%
Carbon Dioxide	99.999%

10.3.2 Ambient Air Ambient air is analyzed once per batch to assess injector performance.

11) Method Calibration

11.1 Initial Calibration

Record the detector temperatures, GC temperature program, standard concentrations, and sample loop volume. All of the following information must be retained to permit reconstruction of the initial instrument calibration: calibration date, test method, instrument, analysis date, each analyte name, analyst's initials, concentration and response, response factor. Refer to Section 16.4 for the acceptance criteria.

11.1.1 Analysis Guidelines

- Analyze differing concentrations covering the desired calibration range by utilizing different sample loops. The dynamic range may be amended as long as all documentation reflects the correct concentrations.
- An ICAL shall be performed at a minimum annually.

11.1.2 Initial Calibration Requirements

Once a set of ICAL standards is analyzed, the previous ICAL may no longer be used to analyze new samples and it must be archived. The only time an archived ICAL can be used thereafter is to review or re-evaluate samples(s) previously processed using that ICAL.

1. A minimum of 5 concentrations, must be used to calculate the calibration curve.
2. Highest concentration, together with the lowest concentration, defines the calibration curve.
3. Lowest concentration must be at or below the method reporting limit.
4. The initial calibration event may not be interrupted by maintenance.
5. Only one value per concentration may be used.
6. Analyze calibration standards from low to high concentration.
7. All ICAL analyses must be completed within 48 hours.
8. One injection per 5 points (2 per 6) may be re-analyzed to replace "bad" injection(s).
9. Point dropping policy:
    - The following are guidelines to follow if points are to be reviewed to determine the appropriateness of dropping a point or injection.
    - Lowest concentration must be at the MRL and may not be dropped unless another concentration is added to the upper end of the curve. This would in turn raise the MRL.
    - Points at the high end may be dropped but another concentration must be added and used in the calculation. The curve range must be noted.

- Points must not be dropped from the "interior" of a curve unless there is an assignable cause* for doing so that affects many (if not all) the analytes in the calibration standard. If a calibration standard is to be dropped from the interior of the curve, all the analytes in the calibration standard must be dropped from all the analytes' calibration curves.
- If a point or a calibration standard is dropped, the reason must be documented (and the results maintained with the documentation for the final ICAL).
- A calibration standard may be re-analyzed if the first analysis of the standard has been dropped and other requirements in this policy are met (i.e., still within 48 hours).
- Once the ICAL has been used to calculate and report sample results, it is not to be changed.

* Assignable causes include

- Standard preparation error
- Instrument malfunction (e.g., it quits acquiring in the middle of the analysis)
- Bad injection or purge

10. A set of concentrations for a calibration curve is in the following table (Attachment 5). However these concentrations might change due to the availability of the standards. Other concentrations can be used as long as all other guidelines for the analysis of initial calibration are followed.

Note: Hydrogen may not be linear; therefore, if an average response factor or linear regression cannot be used, a quadratic curve fit may be employed. A quadratic (second order) model requires a minimum of five calibration points.

11.1.3 ICAL Update Procedure

1. Open most recent method.
2. Save to new ICAL method ID. The date used in method ID is the date files were analyzed.
3. Clear all responses prior to update initiation and/or clear levels if different concentrations are to be used (Initial Calibration → Clear All Calibration Responses; Initial Calibration → Clear All Calibration Levels).
4. Quantitate standard
5. Review all peaks for retention time, integration, etc.
6. Update responses for standard
7. Repeat for all standards
8. If necessary load midpoint standard and update retention times.
9. Save method.
10. Verify Calibration Files listed on Response Factor Report are correct (Both Primary and Secondary Reviewer).
11. Verify responses of Page 3 of Edit Compounds are correct (Both Primary and Secondary Reviewer).
12. Verify file ID, acquisition time, quant time, update time, and last update information is correct on the Calibration Status Report (Both Primary and Secondary Reviewer).
13. Save Method. Confirm that no other copies of the method are open on other computer workstations.

Note: It is also acceptable to quantitate all standards and review all peaks before updating responses but steps 1-2 still must be completed initially. Step 3 also must be done prior to beginning ICAL update.

11.1.4 Initial Calibration Review

The ICAL checklist is used to document the review and approval process. The Analyst's calculation and assessment along with a peer review of all ICAL data and documentation as stated in Attachment 2 is required before the ICAL may be used to analyze samples.

11.1.5 Initial Calibration File

An ICAL file is to be created for each initial calibration performed per instrument into which is placed the following ICAL documents. The file shall remain in the laboratory and be filed by instrument and date.

- ICAL Checklist filled out, reviewed and approved
- Blank analysis quantitation report
- Calibration status report (aka Calibration History)
- Relative Response Factor Report / Percent Relative Standard Deviation
- Plot for quadratic fit for hydrogen, if necessary
- Quantitation report for each calibration standard (including manual integration documentation – before and after manual integration)
- ICV quantitation report and evaluate continuing calibration report (aka Percent Difference Report)
- Injection log (optional)

11.1.6 Initial Calibration Verification Verify the initial calibration by analyzing an independent calibration verification standard (ICV). Utilize the standard described in Section 10.3.1 for the analysis of a second source standard. Refer to Section 16.5 for acceptance criteria.

12) Sample Preparation/Analysis

12.1 Analytical Sequence The analytical batch must be completed for the analysis of ≤20 field samples.

Analytical Sequence Guideline[1]

Sample Description (w/ICAL)	*Sample Description*
Calibration Stds.[2]	CCV[3]
ICV[4]	MB[5]
MB[5]	Lab Air[6]
Lab Air[6]	Samples 1-10[7]
Samples 1-10[7]	CCV[3]
CCV[3]	Samples 11-19[7]
Samples 11-19[7]	LD[8]
LD[8]	LCS[9]
CCV[3]	CCV[3]

[1]The batch QC may be analyzed in an order other than the one listed in this document; the analytical sequence specified below is a guideline.
[2]The initial calibration must be generated in accordance with the guidelines detailed in Section 11.1.1 of this document.
[3]In cases, where the ICAL is not performed the analytical sequence must begin with the analysis of a CCV standard. In an external standard calibration the CCV is to be analyzed no less frequently than every ten samples or every 12 hours, whichever is more frequent, and the analytical sequence is to end with the analysis of a CCV standard.
[4]Every ICAL must be followed by a second source standard (ICV) which contains all of the target analytes. Same source as LCS; therefore, LCS is not required to be analyzed again.
[5]The method blank must be carried throughout the entire analytical process and be analyzed prior to any samples within the sequence. A method blank (MB) shall be run to monitor for laboratory introduced contamination.

[6]A volume of laboratory ambient air shall be analyzed at a rate of one per twenty sample injections or fewer.

[7]EPA Method 3C requires a duplicate injection for each sample. If the samples are being analyzed per a modified Method 3C, they are to be injected once (refer to note number 8). ASTM D 1946 requires only a single injection.

[8]Every batch must include the analysis of a laboratory duplicate. Samples selected for duplicate analysis shall be rotated among client samples. In addition, if performing EPA Method 3C without modification (duplicate injection), the laboratory duplicate analysis will not be necessary. A laboratory duplicate is considered a sample.

[9] A second source standard similar to 10.3.1.1 shall be analyzed once per twenty sample injections or fewer.

12.2 Conditions

The column and detector temperatures should be adjusted to the recommended levels. The column should be conditioned as instructed in Section 9.1.1. Once the GC/TCD system is optimized for analytical separation and sensitivity, the identical sample operating conditions must be used to analyze all samples, blanks, calibration standards and quality control samples.

The recommended settings and system parameters for GC01 are as follows:

Sample Inlet: GC
Injection Source: Sample Loop
Run Time: ~8 min

OVEN

Initial Temperature: 50˚C *Maximum Temperature*: 250˚C
Initial Time: 2.0 min *Equilibration Time*: 0.0 min

Ramps: Rate: 30˚/min
Final Temp.: 200˚C
Final Time: 1 min

COLUMN

Type: Packed
Model: Carbosphere 60/80
Dimensions: 6’ x 1/8”

DETECTOR

Temperature: 260˚C
Reference Flow: 45mL/min
He Make up: 20mL/min

The recommended settings and system parameters for GC20 are as follows:

Sample Inlet: GC
Injection Source: Sample Loop
Run Time: ~6.5 min

OVEN

Initial Temperature: 50˚C *Maximum Temperature*: 250˚C
Initial Time: 1.0 min *Equilibration Time*: 0.0 min

Ramps: Rate: 30˚/min
Final Temp.: 200˚C
Final Time: 0.5 min

COLUMN

Type: Packed
Model: shin carbon ST 100/120
Dimensions: 2 meters 1mm ID

DETECTOR

Temperature: 300˚C
Reference Flow: 20mL/min
He Make up: 2mL/min

12.3 Retention Time (RT) Windows

Retention time windows for each target analyte must be generated whenever there is a major change in instrument conditions including flow rates or when standard analyses result in analyte retention times outside the established windows. The procedure for determining the retention time windows for this method is as follows. However, other approaches may be employed, providing that the analyst can demonstrate that they provide performance appropriate for the intended application. For example, the analyst may use the corresponding retention times from the initial calibration as they may show shifts in RTs due to the volume injected (higher concentrations lead to wider peaks).

1. Make sure that the system is operating reliably and that the system conditions have been optimized for the target analytes in the sample matrix to be analyzed.
2. Make four injections of all applicable standard mixes over a 72 hour period. Make the injections cover the entire 72-hour period or the end result could be windows, which are too tight.
3. Record the retention time for each single component analyte to three decimal places. Calculate the mean and standard deviation of the four absolute retention times for each single component analyte and surrogate
4. If the standard deviation of the retention times for the target compound is 0.000, then additional injections may be included or the use of a default standard deviation of 0.01 minutes.
5. The width of the retention time window for each analyte is defined as ±3 times the standard deviation of the mean absolute retention time established during the 72 hour period. If the default standard deviation of 0.01 is used, the width of the window will be 0.03 minutes.
6. Establish the center of the retention time window for each analyte by using the absolute retention time for each analyte from the continuing calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

Retention time windows must be calculated for each analyte on each instrument. New retention time windows must be established when a new column is installed.

12.4 LOQ Establishment, Verification, and Acceptance Criteria

A) The LOQ must be set within the calibration range (≥ low std. of the current passing ICAL) prior to sample analysis.
B) The LOQ for each analyte must be ≥ the analyte's LOD.
C) Initially a passing demonstration of precision and bias must be performed at the LOQ.
D) Run CCV 2 times at LOQ and:
   1) Evaluate the LOQ for precision and bias using current control chart limits.
   2) Check the signal to noise ratio (S/N) using the software. The S/N ratio must be at least 3:1 for each analyte.
E) If anything fails, verify at higher level and notify reporting. Also, make a note in the ICAL documentation.
F) Turn in all LOQ verification data (quant reports and software reports/checks) to QA (regardless of pass/fail).
G) Verify the LOQ on each instrument quarterly by running the CCV at the LOQ and verifying that ongoing precision and bias requirements are met.

12.5 Continuing Calibration Verification

A continuing calibration check shall be performed at the beginning and end of an analytical sequence and every ten field samples, not to exceed a 12 hour period. The concentration of the calibration verification may be varied within the established calibration range. Refer to Section 16.6 for acceptance criteria.

12.6 Laboratory Control Sample

A second source standard similar to Section 10.3.1.1 shall be analyzed once per closed batch. Refer to Section 16.11 for acceptance criteria.

12.7 Method Blank

A method blank must be analyzed by sampling chromatographic grade helium. Refer to Section 16.8 for acceptance criteria.

12.8 Sample Analysis

Refer to Section 16.10 for the acceptance criteria.

12.8.1 Container Pressurization Sample analysis must be made using the same instrument parameters as that of the calibration standards. Refer to the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters* for the procedure of how containers are to be pressurized prior to analysis. The analyst shall record the appropriate pressures on the Service Request form.

12.8.2 Sample Analysis Sample analysis is performed with the utilization of a sample loop equipped with a pump. If the sample container is not equipped with a sampling valve appropriate for this use, the sample container shall be fitted with an adapter. The dead volume within the adapter shall be evacuated and the sample loop flushed then filled with sample gas. Analyze each sample in duplicate (calculate the percent difference of the calculated concentration of each analysis) unless performing a single injection modification or referencing ASTM D 1946 (refer to Section 12.8.3, #2).

Bottle Vacs use a proprietary quick connect fitting (Micro-QT, Entech Instruments). Each female Micro-QT fitting must be purged after use to remove any remaining sample residue and prevent contamination from subsequent usage. Connect a male Micro-QT fitting to a source of ultrapure or carbon-filtered gas. Adjust the pressure to about 10 psig using an inline regulator. Connect the female fitting for several seconds, then remove and place in an oven kept at 60ºC until the next use. Do not heat the fitting higher than 80ºC.

12.8.3 Sample Re-analysis

1. If the response of any permanent gas analyte in a sample is greater than the response of that analyte in the ICAL (outside the ICAL upper calibration range) the sample shall be reanalyzed using a smaller loop.

   Dilution (i.e. Tedlar bags) would compromise sample integrity with the addition of laboratory air. Guidance in performing dilutions and exceptions to this requirement are given below.

   - The dilution factor chosen should keep the response of the analyte peak for a reported target compound in the upper half of the initial calibration range of the instrument. Additional compounds may be reported as long as they are within the calibration range.

2. If the percent difference between the duplicate injection (analysis without modification) is greater than the acceptance criterion of 5%, the sample must be re-analyzed and repeated until acceptable *consecutive* numbers are achieved.

12.9 Laboratory Duplicate (LD)

If the method is being performed with a single injection modification, then the analysis of a LD is required to show precision. The laboratory duplicate should be rotated among clients, whenever possible. Refer to Section 16.9 for acceptance criteria.

12.10 Manual Integration

The integration for each peak is checked to ensure that it has been integrated properly. Assuming an incorrect automatic integration the analyst shall conduct the manual integration in accordance with the *SOP for Manual Integration Policy* including all documentation and reviews associated with the process. The review shall include the analyst and peer reviewer initialing and dating the manual integration as an indication of acceptability and approval.

12.11 Detection Limits and Limits of Detection

If results are to be reported below the MRL, an MDL study must be performed in accordance with the procedure outlined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.* Method detection limits must be determined annually and each time there is a change in the test method that affects how the test is performed, or when a change in instrumentation is such that it affects the sensitivity of the analysis. The MDL study shall be performed on each instrument for which this method is performed. All supporting data must be approved and retained.

The detection limit shall be used to determine the LOD for each analyte. Once determined on each instrument, the highest LOD (for each analyte from all instrument determinations) shall be used as the uniform LOD.

12.11.1 Performance and Acceptance Criteria

1. Perform Limit of Detection (LOD) verification on all instruments (performing this method) immediately following the MDL study. Spike the LOD at 2-4x the MDL; the spike level establishes the LOD.
2. LOD Acceptance
   - Analyte must be detected reliably and identified by the method-specific criteria and produce a signal that is at least 3 times the instrument's noise level (3:1 signal to noise ratio).
   - It is specific to each combination of analyte, matrix, method and instrument configuration.
   - The LOD must be verified quarterly on each instrument (spiked at LOD) using the criteria listed above.
3. If the LOD verification fails (per #2), repeat the detection limit determination and LOD verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.
4. The laboratory shall maintain documentation for all detection limit determinations and LOD verifications (regardless of pass or fail).

Note: Per the DoD QSM and TNI Standard, it is not necessary to perform a MDL study when results are not to be reported below the LOQ/MRL.

12.12 Ambient Air

An ambient laboratory air sample shall be analyzed once per closed batch (20 or fewer sample injections). Refer to Section 16.7 for the acceptance criteria and corrective action.

12.13 Method Modifications

12.13.1 The following are EPA 3C method modifications:

- Reporting carbon dioxide, methane, nitrogen, and oxygen from a single sample injection.
- Reporting hydrogen and carbon monoxide (these compounds are not included in 3C method).
- Sample results are normalized per ASTM D 1946.
- Use of sample containers other than backfilled Summa canisters.

12.13.2 The modification for ASTM D 1946 is the omission of ethane and ethane.

12.13.3 The column backflush procedure described in method ASTM D 1945-03 is not performed.

12.14 Loop calibration

The loop injection port has a standard loop of approximately 100ul to introduce sample to the instrument. There are other loops that are used to introduce smaller and larger amounts and these are calibrated against the normal loop for a known dilution factor.

12.14.1 Calibration Procedure

A standard of approximately 50000ppm for all analytes is analyzed three times with the normal loop. The area counts for all analytes with the exception of hydrogen are summed for each standard. This summation is averaged of the three standard injections. This procedure is duplicated using another loop. The dilution factor is the ratio of the average area counts of the normal loop divided by the average area counts of the other sampling loop.

For current Loop Ratios see Table 1.

13) Troubleshooting

13.1 Prepare new standards, check instrument maintenance, prepare a new curve as needed, etc. Refer to the corrective actions listed in Section 16 of this SOP for additional troubleshooting details.

14) Data Acquisition

14.1 Data System

Load the appropriate analytical sequence (e.g., J:\GC1\sequence\fxgs_25c.s). Enter the analytical sequence information in the table window, including sample/standard name. Load the appropriate quantitation analytical method (e.g., J:\gc1\methods\"appropriate ICAL"). Run the sequence and analyze the standards and samples in the order specified.

14.2 Storing Electronic Data

The initial calibration data must be stored in a quantitation method (on the server) using a unique filename and may not be overwritten at any time in order to maintain an accurate audit trail. Files shall be named with a two-character notation indicating the compound list and the date of the corresponding initial calibration. In addition, all data files including method blanks, continuing calibration verification, laboratory control samples and client submitted samples files shall be saved in a unique sub-directory on the server. An example of how the analyst must store analytical data is as follows:

Instrument Number/Data/Method ID/yr_month/*.d

* Injection (automatically assigned based on order of injection)

14.3 Sufficient raw data records must be retained of the analysis, instrument calibrations and method detection limit studies. This includes analysis/calibration date, test method, instrument, sample identification, each analyte name, analyst's initials, concentration and response, and standards used for the analysis and calibrations as well as any manual integrations and all manual calculations including sample dilutions. All information entered and reported on the quantitation reports must be complete and accurate.

14.4 The essential information to be associated with analysis, such as computer data files, run logs, etc. shall include: Sample ID code, date and time of analysis (both are required for Tedlar bags since the holding time is 72 hours), instrument operating conditions/parameters (or reference to such data), analysis type, manual integrations,

all manual calculations, analyst's initials, sample preparation (pressure readings and balance gas), standard and reagent origin, sample receipt, calibration criteria, frequency and acceptance criteria, data and statistical calculations, review, confirmation, interpretation, and assessment and reporting conventions.

15) Calculation and Data Reduction Requirements

15.1 Initial Calibration

- Response Factor for each injection (equation number 5)
- Mean Response Factor using all injections (equation number 6)
- Percent Relative Standard Deviation (equation numbers 5,6,7, and 8)

Hydrogen (if quadractic is used):

- Coefficient of Determination (equation number 12)

15.2 Initial Calibration Verification

- Response Factor (equation number 5)
- Mean Area Response (equation number 6)
- Percent Difference (equation number 3)

15.3 Continuing Calibration Verification

- Response Factor (equation number 5)
- Mean Area Response, where necessary (equation number 6)
- Percent Difference (equation number 3)

15.4 Laboratory Duplicate and Method 3C without modification

- Relative Percent Difference (equation number 4)

15.5 Sample Analysis

Sample results must be quantitated from the initial instrument calibration and may not be quantitated from any continuing instrument calibration verification.

All permanent gas results are normalized as dry gas to 99.99% proportionately, in order to reflect the true composition of the sample. It is the practice of the laboratory to normalize results of permanent gas analysis, except under special circumstances that occur where the normalization of the results is not utilized or the normalization procedure is modified. For example, samples containing greater than 0.01% by volume of measured constituents other than permanent gases (for instance high hydrocarbon or sulfur levels) are normalized to 99.99% minus the percent contribution from components other than permanent gases.

- Calculate the average area of the two injections, where necessary (equation number 2)
- Calculate the dilution factor, where necessary (equation number 1)
- Analyte concentration (equation number 9)
- Hydrogen concentration (equation number 14)
- Normalization (equation number 11)

When the analysis of a sample produces permanent gas results whereby the total is significantly less than expected, accounting for experimental error, it is the laboratory's practice to reanalyze the sample in question as well as the laboratory air. This will determine if there is a problem with the analytical system. If there is no problem with the system and the results are the same refer to the following example.

> *If the total of the permanent gas analysis is less than 60.0% by volume and the laboratory is not requested to perform additional analyses, the results would be reported unnormalized. The decisions whether to report the unnormalized results is at the discretion of the analyst and department supervisor.*

15.6 Laboratory Control Sample

- Calculate the percent recovery (equation number 10)

15.7 Calculations

15.7.1 Equation Number 1

Dilution Factor

$$DF = \frac{V_{STD}}{V_S}$$

Where:

DF = dilution factor
V_{STD} = volume of standard loop
V_S = volume of sample loop

15.7.2 Equation Number 2

Average

$$\frac{x + y}{n}$$

where:

x = response from the first injection
y = response from the second consecutive injection
n = number being averaged together

15.7.3 Equation Number 3

Percent Difference, %D,

The %D is used for evaluating ICV and CCV vs. the initial calibration

$$\%D = \frac{C_{CCVorICV} - C_{std}}{C_{std}}(100)$$

where, for any given analyte:

$C_{CCVorICV}$ is the calculated concentration being evaluated
C_{std} is the concentration of the standard used

15.7.4 Equation Number 4

Relative Percent Difference (RPD)

$$\frac{|R_1 - R_2|}{\left(\frac{R_1 + R_2}{2}\right)} x100$$

where:

R_1 First measurement value
R_2 Second measurement value

15.7.5 Equation Number 5

Response Factor (RF)

The response factor, for analyte *x* is given by:

$$RF = \frac{A_x}{C_x}$$

where:

A_x = Area of the analyte in the standard
C_x = Concentration of the analyte in the standard

15.7.6 Equation Number 6

Average (or Mean) RF

$$\overline{RF} = \frac{\sum_{i=1}^{N} RF_i}{N}$$

where:
RF_i are the individual RFs from each injection in the initial calibration curve
N is the number of injections

15.7.7 Equation Number 7

Standard Deviation, SD:

$$SD = \sqrt{\sum_{i=1}^{N} \frac{\left(RF_i - \overline{RF}\right)^2}{N-1}}$$

where:

RF_i are the individual RFs from each concentration level in the initial calibration curve
$\overline{RF}$ Average (or Mean) RF of all injections in the initial calibration curve
N total number of injections

15.7.8 Equation Number 8

Percent Relative Standard Deviation, %RSD:

$$\%RSD = \frac{SD}{\overline{RF}}(100)$$

where:

SD — Standard Deviation calculated in equation number 3

$\overline{RF}$ — Average or Mean RF

15.7.9 Equation Number 9

Concentration (C):

$$C = \frac{Area}{\overline{RF}} \times \frac{D_{SLV}}{A_{SLV}}$$

or

$$C = \frac{\overline{Area}}{\overline{RF}} \times \frac{D_{SLV}}{A_{SLV}}$$

where:

Area — is the area obtained from the chromatogram

$\overline{Area}$ — Mean area for both injections, if performing analysis without modification

$\overline{RF}$ — Average (or Mean) RF of all concentration levels in the initial calibration curve

D_{SLV} — default sample loop volume

A_{SLV} — actual sample loop volume

15.7.10 Equation Number 10

Percent Recovery (%R):

$$\%R = \frac{C}{S} x100$$

where:

C = Concentration of the analyte recovered
S = Spiked amount

15.7.11 Equation Number 11

Normalization
Divide each analyte's calculated concentration (percent) by the percent sum of the permanent gases in the sample and multiply by 99.99 or the adjusted value.

15.7.12 Equation Number 12

Quadratic (Coefficient of Determination)

$$COD = \frac{\sum_{i=1}^{n}(y_{obs} - \bar{y})^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - Y_i)^2}{\sum_{i=1}^{n}\left(y_{obs} - \bar{y}\right)^2}$$

where:

y_{obs} = Observed response (area) for each concentration from each initial calibration standard

$\bar{y}$ = Mean observed response from the initial calibration

Y_i = Calculated response at each concentration from the initial calibration

n = Total number of injections

p = Number of adjustable parameters in the polynomial equation (i.e., 3 for a third order; 2 for a second order polynomial)

15.7.13 Equation Number 13

Quadratic Fit

$R = AX^2 + BX + C$

where:

R = response
X = quantity, ng
A, B and C = are coefficients in the equation

15.7.14 Equation Number 14

Analyte Concentration (using equation number 13)

$$X = \frac{\sqrt{4A(R-C) + B^2} - B}{2A}$$

15.8 Data Review

The analyst must review data on a real time basis for all calibration and QC data. The QC data must be evaluated following the data review checklist in Attachment 3. The data shall be reviewed and the sample results calculated and assessed by one analyst and reviewed by a second qualified analyst. The data review checklist shall be used to document the review process. Once it has been completed, the checklist must be initialed, dated and filed with each job file. Results must not be reported until after they are appropriately reviewed according to this SOP, the *SOP for Data Review and Reporting* and the *SOP for Laboratory Ethics and Data Integrity*.

Initial calibrations must be reviewed in the same manner as QC data with all ICAL documentation retained in a separate file. Refer to the initial calibration checklist in

Attachment 2 for the review guideline. The ICAL file must contain all the pertinent information stated in Section 11.1.5.

15.9 Reporting

The results of each test shall be reported clearly, unambiguously and objectively, and shall include all the information necessary for the interpretation of the test results and all information required by this SOP and the *SOP for Data Review and Reporting*. The following are situations whereby the results shall be reported as being analyzed by Modified EPA Method 3C: single injection, reporting hydrogen and carbon monoxide and if analyzing replicate injections (for 3C without modification) and the samples are submitted in Tedlar bags.

15.9.1 EPA Method 3C Modifications

- Single injection
- Sample container other than backfilled Summa canisters
- Reporting carbon monoxide and /or hydrogen

15.10 Sample Preparation and Analysis Observations / Case Narrative Summary Form

This form, which is included in the *SOP for Laboratory Storage, Analysis, and Tracking* must be generated when there are any specific sample composition information, sample preparation, analysis issues and/or observations. In addition, during the analysis, specific identification information or problems, interferences, calibration issues, flags, and additional/expanded explanation of flags should be added to the form. This form may be modified as long as the sections and basic concepts are reserved.

This form is necessary as a means for documenting any unusual or noncompliant information. This form, among other information, will be reviewed when compiling the final report and case narrative. All information regarding the job shall remain in the file, in order that sufficient documentation is available to recreate the job from sample receipt through preparation, analysis, data reduction, and reporting.

16) Quality Control, Acceptance Criteria, and Corrective Action

16.1 This section of the standard operating procedure contains technical acceptance criteria and preferred corrective actions to data nonconformities. Corrective actions shall follow the procedures outlined in the *SOP for Nonconformance and Corrective Action*, where appropriate.

16.2 To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

16.3 It must be determined if there are any instrumentation problems contributing to out of control QC data and the analyst must determine if this has affected sample results. This being the case, all samples (including QC) that are affected by instrumentation problems must be re-analyzed following any necessary maintenance activity.

16.4 Initial Calibration

16.4.1 Acceptance Criteria

- If a quadratic fit (for hydrogen) is used it should be forced through zero.
- The percent relative standard deviation (%RSD) for the response factors must be ≤15% for all compounds except hydrogen if utilizing a quadratic curve.
- Hydrogen may be fitted to a quadratic curve where the coefficient of determination (COD) shall be ≥0.99.
- The retention time for each point must within 0.06 minutes of the mean RT. However it must be noted that higher injection volumes and/or higher concentrations of any analyte may not meet this criteria, which is acceptable.

16.4.2 Corrective Action

If the initial calibration technical acceptance criteria are not met, inspect the system for possible sources. Check standards and re-analyze (per ICAL policy in Section 11.1.2), if necessary. Also, it may be necessary to perform maintenance or perform other corrective actions to meet the technical acceptance criteria. Attempt another initial calibration and make a notation in the maintenance logbook regarding any maintenance steps taken. If the recalibration does not meet the established criteria, new calibration standards must be made. A demonstration of an in-control system is required before proceeding with the analysis.

16.5 Initial Calibration Verification (ICV) Standard

16.5.1 Acceptance Criteria

- The percent difference for each compound in the ICV must be ≤15%.

16.5.2 Corrective Action

If the ICV does not pass the criteria the standard must be reanalyzed and reevaluated. If reanalysis also fails to produce an acceptable recovery, documented corrective action must be initiated. This may include instrument maintenance, a new ICV standard or the analysis of a new initial calibration curve.

16.6 Continuing Calibration Verification (CCV) Standard

16.6.1 Acceptance Criteria

- The percent difference for each analyte in the CCV must be ≤10%, except hydrogen which must be ≤15%.
- The retention time for each analyte in the standard must be within 0.33minutes of the mean RT (of the corresponding analyte) from the ICAL.

16.6.2 Corrective Action

If the continuing calibration fails to meet expected criterion, the CCV may be reanalyzed (no more than two runs of the CCV standard may be analyzed without documented corrective action, i.e. a notation in the logbook). If the acceptance criterion is still not met, it may be necessary to perform maintenance prior to reanalysis. If routine maintenance does not correct the problem, a new initial calibration must be performed on the instrument.

If the retention time criterion is not met, leak check the system, check the carrier gas cylinders, determine if there has been a loss of pressure in lines. If the analytes do not fall within the generated windows, a new retention time window should be generated.

DoD QSM Requirement: If a CCV fails, the laboratory must immediately analyze two additional consecutive CCVs (immediately is defined as within one hour).

- Both of these CCVs must meet acceptance criteria in order for samples to be reported without reanalysis.
- If either of these two CCVs fail or if the laboratory cannot immediately analyze two CCVs, the associated samples cannot be reported and must be reanalyzed.
- Corrective action(s) and recalibration must occur if the above scenario fails. All affected samples since the last acceptable CCV must be reanalyzed.
- Flagging data for a failed CCV is only appropriate when the affected samples cannot be reanalyzed. The laboratory must notify the client prior to reporting data associated with a failed CCV.

16.7 Ambient Air

16.7.1 Acceptance Criteria

- The sum of the results for nitrogen and oxygen/argon must fall between 90% and 110% (un-normalized).

16.7.2 Corrective Action

Reanalyze the lab ambient air and if the results still do not meet the criterion, the sample line should be purged with nitrogen to release any blockage. This is particularly important if the results for the first criterion are low. Also, if the result is low the system should be checked for leaks. All standards, samples and QC samples associated with the lab ambient air should be reanalyzed following the maintenance activity if it is determined that the results could have been affected.

16.8 Method Blank

16.8.1 Acceptance Criteria

- The method blank result for any target analyte must not be greater than the method reporting limit. Also, the blank should not contain additional compounds with elution characteristics that would interfere with identification and measurement of a target analyte.
- For DoD samples, the method blank will be considered to be contaminated if:

  1. The concentration of any target analyte in the blank exceeds 1/2 the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);
  2. The concentration of any common laboratory contaminant in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
  3. The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

  The laboratory shall evaluate whether reprocessing of the samples is necessary based on the above criteria.

16.8.2 Corrective Action

Re-inject the method blank and if the results are the same, analyze an instrument blank (inject without turning on the pump) to determine if the contamination is the blank canister or the analytical system. Corrective action documentation must be initiated following a failed second analysis. If the system is contaminated, then both the method blank(s) and the associated samples in question must be re-analyzed.

16.9 Laboratory Duplicates (Modified EPA Method 3C)

16.9.1 Acceptance Criteria

- Every batch of twenty or fewer samples, if performing EPA Method 3C with modification, must include the analysis of a laboratory duplicate as a measurement of method precision. Refer to Attachment 4 of this document.

16.9.2 Corrective Action

If the replicate results do not fall within the technical acceptance window, the sample should be re-analyzed. If the results are still unacceptable and there does not appear to be any matrix effects, interfering peaks, or instrument problems,

the results for both injections shall be reported to the client with the appropriate qualifier.

16.10 Sample Analysis

16.10.1 Acceptance Criteria

- Samples out of holding time must be handled according to Section 16.12.
- The sample replicate injections are acceptable when the RPD is within ±5% (analysis without modification must consist of consecutive injections).
- Analyte retention time must be within the daily RT window and within 0.33minutes of the mean RT in the ICAL.

16.10.2 Corrective Action

Analysis Without Modification If the two injections do not agree, run additional samples until consistent area data are obtained in two consecutive injections.

Analysis With or Without Modification If the retention time for any analyte falls outside of the retention time window from the latest daily calibration or average initial calibration retention time, the system must be inspected for a change in the head pressure and the results evaluated and reported accordingly.

Results not bracketed by initial instrument calibration standards (within calibration range) must be reported as having less certainty, e.g., defined qualifiers or flags.

16.11 Laboratory Control Sample (LCS)

16.11.1 Acceptance Criteria

- The percent recovery must fall within the fixed recoveries of 85-115% or laboratory generated control limits when available. Refer to Attachment D.

16.11.2 Corrective Action

If the LCS criteria are not met, determine whether the cause is instrumentation problems, result of poor injection or a poor LCS. If necessary perform maintenance, re-inject the LCS or make a new standard. If the LCS criteria are still not met, a new ICAL must be run or the data must be qualified.

16.12 Expired Sample Holding Time

The customer shall be notified by the Project Manager (best attempt) when informed by an Analyst, Team Lead or SMO that the sample's holding time was missed. The customer must decide if the sample analysis shall continue. The documentation of missed holding time and the client's decision to proceed must be included in the corresponding job file. A statement dictating all holding time occurrences must accompany the sample results in the final report.

17) Data Records Management

17.1 All data resubmittal forms and job documentation including Service Requests, Chain of Custody forms, Sample Acceptance Check forms and hardcopy electronic mail messages must be filed in the project file. Final reports, revised reports, and final invoices are stored electronically.

17.2 All laboratory and client documentation must be retained for a minimum of five years.

18) Contingencies for Handling Out of Control Data

18.1 To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control

measure shall be reported with the appropriate data qualifier(s) as detailed in Appendix D of the most current Quality Assurance Manual.

18.2 When analysis quality control results are unacceptable:

If the associated samples are within holding time, re-analyze the sample with criteria under control. Alternatively, evaluate the effect on the sample results and report the results with qualifiers and/or discuss in the case narrative if the effect is judged insignificant.

18.2.1 Method Blank If an analyte in the method blank is found to be unacceptable and the analyte is also found in associated samples, those sample results shall be "flagged" in the report. If the analyte is found in the blank but not in the sample and all other quality control meets acceptance criteria then the results for the sample may be reported without a qualifier. However, if other QC is out of control then an evaluation must be made and the results reported accordingly.

18.2.2 Laboratory Duplicate (Analysis with Modification) If the results from the reanalysis are unacceptable, and there does not appear to be any matrix effects, interfering peaks, or instrument problems, the results for both injections shall be reported to the client. In addition, other results from the same analytical sequence should be reported with the appropriate qualifier.

18.2.3 Laboratory Control Sample An unacceptable LCS must be evaluated along with the sample analysis and reported accordingly.

18.2.4 Initial Calibration Sample data may NOT be reported with an unacceptable ICAL.

18.2.5 CCV Sample data associated with an unacceptable calibration verification may be reported as qualified data under the following special condition:

When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. Otherwise the sample affected by the unacceptable CCV shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

18.3 Sample Out of Control

18.3.1 Hold Time All Tedlar bag samples analyzed outside of the required hold time of 72 hours must be reported with the appropriate qualifier.

18.3.2 Retention Time All analytes outside of the retention time window (following a retention time evaluation) must be reported with the appropriate qualitative uncertainty, where necessary.

18.3.3 Duplicate Results (Analysis without modification) If the results from any of the repeated injections are still unacceptable (and other sample results were acceptable), and there does not appear to be any matrix effects, interfering peaks, or instrument problems, the results for both injections shall be reported to the client. If the out-of-control results are due to matrix interferences, report the results with a matrix interference qualifier.

19) Method Performance

19.1 An on-going assessment of method performance is conducted in order to ensure that the laboratory is capable of reporting results which are acceptable for its intended use. Validation of the method is confirmed by the examination and provision of objective evidence that these requirements are met.

19.2 Method Detection Limit (MDL)

The procedure used to determine the method detection limits are as stated in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as defined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation*.

The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. MDLs can be obtained using standards at a concentration of about 300ppm to 1000ppm and making at least seven replicate measurements of the compounds of interest, computing the standard deviation, and multiplying this value by the appropriate Student's t value for 99 percent confidence.

The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. Refer to Section 12.11.1 for the LOD verification criteria.

Note: Per the DoD QSM and TNI Standard, it is not necessary to perform a MDL study when results are not to be reported below the LOQ/MRL.

19.3 Accuracy and Precision

Refer to Section 16.9 for information on replicate precision criteria for method performance. Single laboratory accuracy is presented as the second source initial calibration verification standard, which meets the method performance criteria of 15%. Additionally, laboratory generated control limit data for LCSs are presented for the analytes of interest and may be referenced in attachment 4. Refer to Section 12.4 for the accuracy and precision LOQ requirements.

19.4 Demonstration of Capability

This laboratory has continuously performed this method since before July 1999. Ongoing demonstration of capability shall be performed and documented; however, the initial demonstration of method capability is not required.

19.5 Proficiency Testing (PT) Program

Proficiency testing samples are not available from a third party for this method. Repeatability studies will be performed biannually to meet the DoD QSM proficiency testing requirements. A minimum of eight QC analyses performed over multiple days or on the same day will be compiled. Statistical validity will be assessed by evaluating results against LCS control limits and an RSD of 15%.

20) Summary of Changes

Table 20.1

Revision Number	Effective Date	Document Editor	Description of Changes
14.0	12/31/16	C. Humphrey	Approval Page - Updated
			7.3 – Changed "DoD QSM 5.0" to "DoD QSM"
			10.3 – Updated to align with current requirement
			10.3.1.3 – Added Carbon Monoxide
			12.11.1 – Changed "DoD QSM 5.0" to "DoD QSM" under Note
			16.6.2 – Changed "DoD QSM 5.0 Requirement" to "DoD QSM Requirement"
			19.2 - Changed "DoD QSM 5.0" to "DoD QSM"
			19.5 – New section
			Attachment 4 – Updated control limits

21) References and Related Documents

21.1 "*Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen from Stationary Sources*", EPA Method 3C

21.2 ASTM D 1946-90 (Reapproved 2006), "*Standard Practice for Analysis of Reformed Gas by Gas Chromatography*".

21.3 ASTM D 1945-03 (Reapproved 2010), "*Standard Test Method for Analysis of Natural Gas by Gas Chromatography".*

21.4 *Department of Defense Quality Systems Manual for Environmental Laboratories*, Version 5.0, July 2013.

21.5 *SOP for Batches and Sequences*, SOP ID ADM-BATCH_SEQ

21.6 *SOP for Making Entries onto Analytical Records*, SOP ID CE-QA007

21.7 *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation*, SOP ID CE-QA011

21.8 *SOP for Manual Integration Policy*, SOP ID CE-QA002

21.9 *SOP for Nonconformance and Corrective Action*, SOP ID CE-QA008

22) Appendix

22.1 Tables

Table 1 – Loop Ratios

22.2 Attachments

Attachment 1 – Training Plan

Attachment 2 – Initial Calibration Checklist

Attachment 3 – Data Review Checklist

Attachment 4 – MRLs and Control Limits

Attachment 5 – Calibration Curve Concentrations

Table 1

Loop Ratios	
Normal Loop	1.00
Small Loop	0.1556
Medium Loop 1	0.4202
Medium Loop 2	0.8521
Large Loop	1.280

Note: New loop ratios may be established prior to the revision of this document, refer to the most recent loop ratios.

Attachment 1

Training Plan

Training Plan for Analysis of Fixed Gases by GC/TCD

Trainee _____ Trainer _____ Instrument _____

1. Read SOP Trainer ____ Trainee ____ Date _____
2. Read Method: EPA Method 3C, ASTM D 1946, ASTM D 1945 Trainer ____ Trainee ____ Date _____
3. Demonstrated understanding of the scientific basis of the analysis

   Gas chromatography Thermal Conductivity Detector Trainer ____ Trainee ____ Date _____
4. Demonstrated familiarity with related SOPs Trainer ____ Trainee ____ Date _____
   SOP for Batches and Sequences
   SOP for Making Entries onto Analytical Records
   SOP for Manual Integration Policy
   SOP for Significant Figures
   SOP for Nonconformance and Corrective Action
   SOP for Performing MDL Studies and Establishing Limits of Detection and Quantitation
5. Observe performance of SOP Trainer ____ Trainee ____ Date _____
   ___standard preparation
   ___sample preparation (gas-phase dilutions)
   ___analytical sequence setup
   ___initial calibration and initial calibration verification
   ___continuing calibration verification
   ___sample analysis
   ___EnviroQuant introduction
   ___data reduction and reporting
6. Perform SOP with supervision Trainer ____ Trainee ____ Date _____
   ___standard preparation
   ___sample preparation (gas-phase dilutions)
   ___analytical sequence setup
   ___initial calibration and initial calibration verification
   ___continuing calibration verification
   ___sample analysis
   ___EnviroQuant use
   ___data reduction and reporting
7. Independent performance of the SOP Trainer ____ Trainee ____ Date _____
   ___standard preparation
   ___sample preparation (gas-phase dilutions)
   ___analytical sequence setup
   ___initial calibration and continuing calibration verification
   ___sample analysis
   ___EnviroQuant proficiency
   ___data reduction and reporting
   ___initial demonstration of competency
      ___ Four consecutive laboratory control samples
8. Instrument operation and maintenance Trainer ____ Trainee ____ Date _____
   ___gas chromatograph and column installation (packed)
   ___detector (TCD) setup and maintenance
   ___data system

Attachment 2

Initial Calibration Checklist

Initial Calibration Checklist (Fixed Gases)

Analysis: EPA Method 3C / ASTM D 1946 / ASTM D 1945

ICAL Date _____ Instrument ☐ GC01 ☐ GC _____

Analyst		Reviewer
☐	1. Is the required documentation in the ICAL file?	☐
	☐ Sequence report	
	☐ Blank analysis Quantitation Report	
	☐ Calibration Status Report (aka Calibration History) – Initial	
	☐ Response Factor Report and Plot for Hydrogen	
	☐ Quantitation Report for each calibration standard (including manual integration documentation – before and after printouts)	
	☐ ICV Quantitation Report and Evaluate Continuing Calibration Report (aka Percent Diff. report)	
☐	2. Was the ICAL performed continuously (i.e., not interrupted for maintenance or sample analysis)?	☐
☐	3. All the calibration standards analyzed within 48 hours of each other?	☐
☐	4. Were the standards analyzed from low concentration to high concentration?	☐
☐	5. Are all the analytes in the blank analysis < MRL?	☐
☐	6. Does each analyte's ICAL include a minimum of 5 consecutive concentrations?	☐
☐	7. Was each standard concentration included in the ICAL?	☐
☐	8. If a point is dropped, is information noted in the ICAL explaining the reason?	☐
☐	9. Does this follow the Laboratory's point dropping policy? Are the injections dropped for that concentration for each analyte?	☐
☐	10. For each analyte, is the lowest standard's concentration at or below the analyte's MRL?	☐
☐	11. For each analyte, are there no levels skipped?	☐
☐	12. For analytes calibrated using RF, is the RSD ≤15%? For Hydrogen ≥0.99?	☐
☐	13. For the ICV analysis, is the percent recovery for each analyte 85-115%?	☐
☐	14. Are all peak integrations including manual integrations (per *SOP for Manual Integration Policy*) acceptable? *If so, initial and date the appropriate pages.*	☐

COMMENTS:

_____

_____

_____

_____

Analyst _____ Secondary Reviewer _____

Date _____ Date _____

Attachment 3

Data Review Checklist

Fixed Gases per EPA Method 3C / ASTM D 1946 / ASTM D 1945
Data Review Checklist
(Note exceptions and include Sample Preparation and Analysis Observations / Case Narrative Summary Form as appropriate)

Analysis Date _____ Instrument ☐ GC1 ☐ GC20

Client _____ QC Level _____

Project # _____ Due Date _____

Modification ☐ Yes ☐ No

Analyst **Reviewer**

Initial Calibration

☐ 1. Is the referenced ICAL the most recent ICAL performed? ..... NA

☐ 2. Has the referenced ICAL been peer reviewed and all associated documentation including the ICAL review checklist available for review? ..... NA

☐ 3. Were all associated requirements within the specified limits? ..... NA

Data

☐ 1. Is the sample data documentation present and correct? ..... ☐
- ☐ Sample raw data?
- ☐ All target analyte responses within calibration range?
- ☐ All peak integration acceptable?
- ☐ All manual integrations flagged and documented (before and after)? If so, initial and date.
- ☐ All analyte retention times within the generated RT window?
- ☐ All calculations correct?
- ☐ First quantitation report initialed and dated by analyst?

☐ 2. Do all sample duplicate injections (if analyzing without modification have a RSD ≤5%? ..... ☐

☐ 3. CCV have a percent difference of ≤10% (≤15% for hydrogen)? ..... ☐

☐ 4. Is the retention time (for CCV) for each analyte in the standard within 0.33min from the mean RT (of the corresponding analyte) from the ICAL? ..... ☐

☐ 5. Is the sum of the gases in the lab air within 90% and 110%? ..... ☐

☐ 6. Are the %R for the LCS within the acceptance criteria for each analyte? ..... ☐

☐ 7. Are the analytes in the MB < MRL? ..... ☐

☐ 8. Do all reported analytes fall within the generated retention time windows? If not, is the reason for reporting analyte in the sample documented? ..... ☐

☐ 9. Is the RPD (with modification) for the LD within the laboratory generated RPD limits? ..... ☐

☐ 10. **DOD: Are manual integrations notated in the case narrative**? ..... ☐

COMMENTS:

_____

_____

_____

☐ LIMS Run Approval ☐ LIMS Supervisor Approval

Analyst _____ Secondary Reviewer _____

Date _____ Date _____

(Checklist Revised 05/18/16)

Attachment 4

Method Reporting Limits and Control Limits

Target Analytes with Associated MRLs

Compound	Method Reporting Limit
Hydrogen	1000ppm
Oxygen	1000ppm
Nitrogen	1000ppm
Carbon monoxide	1000ppm
Methane	1000ppm
Carbon dioxide	1000ppm

Laboratory Generated Control Limits – ASTM D 1946-90 / Modified EPA 3C Single Injection

Analyte	LCS - LCL (%R)	LCS - UCL (%R)	LD (RPD)
Hydrogen – H_2	94	105	3
Oxygen – O_2	97	108	3
Nitrogen – N_2	89	113	7
Carbon monoxide - CO	98	108	3
Methane – CH_4	94	111	3
Carbon dioxide – CO_2	94	104	3

Note: New limits may be established prior to the revision of this document, refer to the most recent control limits.

Attachment 5

Calibration Curve Concentrations

Suggested Calibration Curve Concentrations (ppm unless noted as %)

ICAL	Hydrogen	Oxygen	Nitrogen	Carbon Monoxide	Methane	Carbon Dioxide
1	373.69	467.11	466.18	470.85	373.69	467.11
2	2000	2500	2495	2520	2000	2500
3	7473.77	9342.21	9342.21	9379.58	7511.14	9323.53
4	40000	50000	50000	50200	40200	49900
5	467731.47	584664.34	584664.34	587002.99	470070.13	583495
6	99.999%					
7		99.999%				
8			99.999%			
9					99.999%	
10						99.999%

ICAL	Amount of Standard Spiked onto Instrument
1	small loop injection of a 2500ppm/2000ppm standard [1,2]
2	standard loop injection of a 2500ppm/2000ppm standard [1,2]
3	small loop injection of a purchased 5%/4% standard (see section 10.3.1.1) [2]
4	standard loop injection of a purchased 5%/4% standard (see section 10.3.1.1) [2]
5	large loop injection of a purchased 5%/4% standard (see section 10.3.1.1) [2]
6 through 10	standard loop injection of neat gas compounds (see section 10.3.1.1)

[1]2500ppm/2000ppm standard is made by introducing 600ml of a purchased 5%/4% standard into a 6 liter summa canister and pressurized to +14.7psig (29.4psi) with helium.
[2]The loop injection volumes are calculated as described in section 12.14 and shown in Table 1.

Calibration Range	
Hydrogen	1000ppm – 99.999%
Oxygen	1000ppm – 99.999%
Nitrogen	1000ppm – 99.999%
Carbon Monoxide	1000ppm – 58.700%
Methane	1000ppm – 99.999%
Carbon Dioxide	1000ppm – 99.999%

DETERMINATION OF AIR-PHASE PETROLEUM HYDROCARBONS (APH) BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

DOCUMENT I.D. VOA-MAPH

Approved By: Kate Kaneko Date: 5/23/18
Interim Laboratory Director – Kate Kaneko

Approved By: Chaney Humphrey Date: 5/23/18
Quality Assurance Manager – Chaney Humphrey

Approved By: Date: 5/22/18
Technical Manager (Volatile GC/MS) – Chris Parnell

Doc Control ID:	Uncontrolled	Archived Date:	

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1) Scope and Applicability

1.1 This procedure is based on and incorporates the requirements detailed in the Method for the Determination of Air-Phase Petroleum Hydrocarbons (APH), Revision 1, December 2009, Massachusetts Department of Environmental Protection. It is designed to measure the gaseous-phase concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in air. Volatile aliphatic hydrocarbons are collectively quantitated within two carbon number ranges: C5 through C8 and C9 through C12. In addition, volatile aromatic hydrocarbons are collectively quantitated within the C9-C10 range. Also, this method may be used to measure the individual concentrations of target APH analytes 1,3-butadiene, methyl-tert-butyl ether (MtBE), benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, and naphthalene in air. An extended list of target analytes also may be reported since this method overlaps with EPA Method TO-15.

1.2 This method typically applies to whole air samples received in Summa stainless steel canisters, with subsequent analysis by gas chromatography/mass spectrometry (GC/MS). The method reporting limit (MRL) for this method for each of the collective aliphatic and aromatic fractional ranges is approximately 2.5 – 20ug/m3. The MRL for the target APH analytes is compound specific but is approximately 0.50ug/m3. Refer to the most recent method detection limit study and initial calibration for the corresponding method detection and reporting limits. The reported MRL may be adjusted higher; however, the capability of achieving lower MRLs for specific project requirements must be thoroughly demonstrated and documented. The number of samples that may be analyzed in a 24-hour period is about twenty.

2) Summary of Procedure

2.1 Samples are collected in pre-cleaned, evacuated Summa stainless steel canisters. An aliquot of an air sample is concentrated on a solid adsorbent trap to collect the analytes of interest. To remove co-collected water vapor, the concentrated sample then goes through a water removal (dry purge) step. After the sample is pre-concentrated on a trap, the trap is heated and the APHs are thermally desorbed onto a refocusing cold trap. The APHs are then thermally desorbed onto the head of a capillary column once the cold trap is heated. The oven temperature (programmed) increases and the APHs elute and are detected by the mass spectrometer. The GC/MS utilizes a linear quadrupole system, which allows for it to be operated by either continuously scanning a wide range of mass to charge ratios (SCAN mode) or by Select Ion Monitoring mode (SIM), which consists of monitoring a small number of ions from a specified compound list.

2.2 Target APH analytes are identified and quantitated using characteristic ions. Collective concentrations of C9-C10 aromatic hydrocarbons are quantitated using extracted ions. Collective concentrations of aliphatic hydrocarbons fractions are quantitated using a total ion chromatogram, subtracting out target APH analytes and C9-C10 aromatic hydrocarbons. The target analytes will be quantitated and reported using EPA method TO-15. Since the sample pre-concentration steps and analytical conditions are identical for TO-15 and the Massachusetts APH method, all sample results can be generated from the same analytical run.

3) Definitions

3.1 Cryogen A refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Liquid nitrogen (cryogen) is used for this purpose and it has a boiling point of -195.8°C.

3.2 Gauge Pressure Pressure measure with reference to the surrounding atmospheric pressure, usually expressed in units of psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

3.3 MS-SCAN Mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

3.4 Analytical Sequence The analytical sequence describes exactly how the field and QC samples in an analytical batch are to be analyzed.

3.5 Stock Standard A purchased, multi-component gas-phase mixture having certified concentrations, used to prepare working calibration standards.

3.6 Working Calibration Standard A gas-phase mixture of all the target analytes at a known concentration prepared by diluting a gas-phase stock standard into a canister. Used for calibrations. Standard canisters prepared from methanol stocks are not allowed.

3.7 Calibration or Standard Curve A calibration or standard curve is a graph which plots the concentration of a compound (or an analyte) versus the instrument response to the compound.

3.8 Initial Calibration Verification (ICV) Standard A gas-phase standard prepared in the laboratory containing known concentration(s) of analytes of interest. It is prepared from gas-phase stock standards which are from a different source than the standards used to prepare the working calibration standards. Standard canisters prepared from methanol stocks are not allowed.

3.9 Continuing Calibration Verification (CCV) Standard A working calibration standard which is analyzed at specific intervals in order to verify that the instrument continues to meet the calibration criteria.

3.10 Field Sample A sample collected and delivered to the laboratory for analysis.

3.11 Manual Integration This term applies to a data file in which setpoints have been changed and reintegration has occurred under the changed setpoints; baselines have been adjusted; peak integration start and stop “ticks” have been changed; peak area, or peak height, are changed after the time of data collection and data file generation.

3.12 Batch Quality Control (QC) Batch QC refers to the QC samples that are analyzed in an analytical batch of field samples and includes the Method Blank (MB), Laboratory Control Sample (LCS) and Laboratory Duplicate (LD).

3.13 Internal Standard Calibration Compares the instrument responses from the target compound in the sample to the responses of specific standards (called internal standards), which are added to the sample or sample preparation prior to analysis. The ratio of the peak area (or height) of the target compound in the sample or sample preparation is compared to a similar ratio derived for each calibration standard.

3.14 May This action, activity, or procedural step is neither required nor prohibited.

3.15 Must This action, activity, or procedural step is required.

3.16 Shall This action, activity, or procedural step is required.

3.17 Should This action, activity, or procedural step is suggested, but not required.

3.18 Service Request A form generated, at the time of sample receipt, which details pertinent information such as client name, address, contact, client and laboratory sample identifications, sampling and receipt dates and times, requested analyses, sample type,

canister pressures (initial and final), and the service request number (unique number for each submitted job) and serves as an inter-laboratory "custody" form which accompanies all samples throughout the laboratory.

3.19 Air-Phase Petroleum Hydrocarbons (APH) These are defined as collective fractions of hydrocarbons compounds eluting from isopentane to n-dodecane, excluding target APH analytes. APH is comprised of C5-C8 aliphatic hydrocarbons, C9-C12 aliphatic hydrocarbons, and C9-C10 aromatic hydrocarbons.

3.20 APH Component Standard A mixture of the aliphatic and aromatic compounds listed in Table 4. The compounds comprising the APH Component Standard are used to define and establish the retention time windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and determine average chromatographic response factors that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges. The APH target analytes are in a separate stock standard cylinder (also used for EPA Method TO-15) and are prepared as separate working standards in canisters.

3.21 Laboratory Control Sample A humidified canister fortified with a gaseous-phase mixture of the APH Component Standard obtained from a different stock solution than the APH working/calibration standards.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP may perform analysis, and interpretation of the results. The analyst must also ensure that a second analyst that is familiar with this analysis reviews the results and all applicable QC.

4.2 The supervisor/manager must ensure that method proficiency is documented initially and whenever significant changes in the instrument type, personnel, matrix or test method are made.

4.3 The department supervisor/manager or designee shall perform final review and sign-off on the data.

5) Interferences

5.1 Canisters Canisters should be stored in a contaminant free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample. The pressure/vacuum is checked prior to shipment and upon receipt from the field. Any problems with the sample from the field are noted on the service request form and the Project Manager contacted.

Also, canisters must be cleaned and certified to be free from target analytes before being shipped to the field for sample collection. The procedure is described in detail in the *Standard Operating Procedure for Cleaning and Certification of Summa Canister and Other Specially Prepared Containers* (refer to this procedure as well as Section 11.9.1 for the acceptance criteria.).

5.2 Analytical System The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air

blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with buna-N rubber components must be avoided.

5.3 Glassware Interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware results in discrete artifacts and/or elevated baselines in the detector profiles should be minimized. All glassware associated with this method must be scrupulously cleaned to avoid possible contamination. The cleaning shall be performed in accordance with the procedure outlined in the *SOP for Glassware Cleaning*. The use of high purity water, reagents, and solvents helps to minimize these problems.

5.4 Organic Compounds Certain organic compounds not associated with the release of petroleum products, including chlorinated solvents, ketones and ethers will be detected by this method and quantified within an aliphatic or aromatic hydrocarbon range. *When noted by the analyst, the identification and/or quantitation of such compounds must be disclosed on the laboratory report.* Non-APH compounds may be subtracted out of the hydrocarbon ranges before reporting results. When requested by the data user the identification of such non-APH compounds must be disclosed on the laboratory report or case narrative.

6) Safety

6.1 Refer to the laboratory's Environmental, Health and Safety Manual as it makes reference to the safe handling of chemicals, Safety Data Sheet (SDS) location, and the laboratory waste management plan for the safe disposal of chemicals and samples.

6.2 This procedure may include CHEMICAL, OPERATIONAL and/or EQUIPMENT hazards. Employees must review and understand the following hazards and their preventive measures prior to proceeding with this activity.

HAZARD ASSESSMENT		
Job Task #1: Standard and Sample Preparation	**Hazards**	**Preventative Measures**
Compounds, mixtures of compounds, standards, surrogates, and samples.	Exposure to potential health hazards through absorption through skin. Inhalation hazards.	Reduce exposure through the use of gloves and fume hoods. Safety glasses must be worn when working in the prep lab. Care should be taken when handling standard material in a neat or highly concentrated form. Personal protective clothing (safety glasses, gloves, and lab coat) are required when handling standard material in neat form. Consult Safety Data Sheets (SDS) for compounds being handled in this procedure, and be familiar with proper safety precautions.
Job Task #2: Working with Liquid Nitrogen	**Hazards**	**Preventative Measures**
Turning valves and handling tubing and fittings that have been in contact with the cryogen.	Can cause serious tissue damage (frostbite) with only a few seconds of contact.	Wear neoprene or leather gloves. Valves on cryogen dewars should be opened slowly so leaky fitting can be identified.
Job Task #3: Working with Pressurized Gases	**Hazards**	**Preventative Measures**
Using and moving compressed gas cylinders.	Gas leak, fire, and explosion. Personal injury due to falling during transport.	All cylinders must be secured in an upright position to a wall or immovable counter with a chain or a cylinder clamp when not in use. Keep safety caps on when cylinders are not in use. A handcart must be used when transporting cylinders. The cylinder must be secured to the handcart with a chain or belt. The regulator should never remain on small "D" size cylinders following use. Full cylinders must be kept separate from empty cylinders. Flammable gases (i.e. pressurized hydrogen) must be clearly labeled. Flammables and oxidizers must be separated by a ½-hour fire wall or by at least twenty feet.
Job Task #4: Glass Syringes	**Hazards**	**Preventative Measures**
Glass syringe use	Skin lacerations and punctures.	The proper use of syringes should be part of employee training for this SOP. Care should be taken to avoid personal injury as a result or improper handling techniques.

Hazard information related to this activity which is not included or referenced in this document, should be immediately brought to the attention of the Department Supervisor.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Air samples are collected in the field and delivered to the laboratory and should be collected in a specially prepared, leak-free, passivated stainless steel canister (with valve) of desired volume (e.g., 6L). It is also acceptable to use Bottle Vacs (Entech Instruments, Simi Valley, CA) which are specially treated amber glass bottles fitted with a fused silica-coated valve (typically one liter volume). The use of Tedlar bags is considered a modification and is discouraged due to the inherent chemical artifacts which can interfere with the analysis.

7.2 Time-integrated samples require the use of a properly calibrated flow controller (refer to the Standard Operating Procedure for Flow Controllers and Critical Orifices). The flow controller must be calibrated prior to sample collection. Upon receipt at the laboratory, a post sampling calibration check must be performed on the flow controller. The relative percent difference (RPD) between the initial and post sampling calibration readings must be calculated. As long as the RPD is ≤20%, the calibration is considered to still be valid and thus the sample collection interval is also assumed to be valid. If the RPD is >20%, consideration must be given to whether resampling is necessary to achieve data quality objectives. If the sample is analyzed, a notation must be provided on the data reporting sheet and case narrative disclosing the RPD value.

7.3 There are no special preservation requirements for canisters. Canisters should be stored on the appropriate shelves until they are to be analyzed. The required holding time for samples in canisters for this method is 30 days.

8) Apparatus and Equipment

8.1 Gas Chromatograph (GC) An instrument capable of temperature programming, with a column oven that may be cooled to sub-ambient temperature at the start of the gas chromatographic run to result in the resolution of the VOCs.

8.2 Autosampler

Teledyne-Tekmar AutoCan Autosampler:	14-ACAN-074
Concentrating Trap (cryogenic trap, built-in):	14-6938-020
Cryofocusing Module w/split valve:	14-6520-A00
GAST Vacuum Pump:	DOA-P104-AA

8.3 Mass Spectrometer (MS) A MS capable of scanning from 33 to 350 amu every second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Bromofluorobenzene (BFB) which meets all of the criteria when 50ng or less of BFB is injected onto the GC/MS system.

8.3.1 Ionization Gauge Controller

Granville-Phillips 330 Ionization Gauge Controller:	330001/2/3
Hewlett Packard Ionization Gauge Controller:	59864B

8.4 Analytical Column

Restek Rxi-1ms Fused Silica Capillary Column
60m x 0.25mm ID
1.0 micron film thickness

NOTE: Based upon data obtained from the MADEP VPH Round Robin testing programs, the choice of chromatographic column may have a significant impact on the apportionment

and quantitation of aliphatic and aromatic compounds within the fractional ranges specified in this method. Substitution of the required column is not allowed, unless it can be demonstrated that the selected column has equivalent chromatographic properties and elution order for the aliphatic and aromatic compounds and ranges of interest.

To demonstrate equivalency of column chromatography, a mid-range calibration standard must be analyzed on both the required column and the proposed substitute column, with all other run and system parameters held constant. The concentrations of C5-C8 and C9-C12 aliphatic hydrocarbons, C9-C10 aromatic hydrocarbon ranges and target analytes must be determined for each column. The relative percent difference between the concentrations of each hydrocarbon range and target analyte, excluding naphthalene, obtained from each column must be ≤25. The RPD for naphthalene must be ≤40. The elution order of APH Components on the proposed substitute column must be equivalent to the elution order on the required column.

8.5 Data Systems IBM-compatible PC with Windows 95/98/NT/XP and Hewlett Packard Chemstation software including EnviroQuant with Extracted Ion Current Profile (EICP), National Institute of Standards and Technology (NIST) library or equivalent.

8.6 Canister Pressurization Station Vacuum/Pressure Gauge [0 to –30 in Hg; 0-90 psig]

8.7 Canister Sampling Devices VICI Condyne Model 300 Flow Controller

8.8 Gas Collection Devices

- Lab Commerce, Aerosphere Model S6L, 6.0L Passivated Stainless Steel Canisters or equivalent
- Lab Commerce, Stabilizer Model 22.4L, 2.4L Canisters or equivalent
- Restek Corporation, #24203, 3.0L Silco Canisters or equivalent
- Entech Instrument, Silonite™ Canisters or equivalent
- Entech Instruments, Bottle Vacs or equivalent

9) Standards, Reagents, and Consumable Materials

9.1 Reagents

9.1.1 UHP Grade Helium (99.999%)(GC carrier gas and preconcentrator purge/sweep gas)
9.1.2 Cryogen - Liquid nitrogen (used to cool preconcentrator traps)
9.1.3 UHP/Zero Grade Air
9.1.4 ASTM Type II Water or equivalent
9.1.5 High purity grade methanol

9.2 Standards

9.2.1 Instrument Performance Check, Internal Standard and Surrogate Spiking Mixture Prepare a standard solution of p-Bromofluorobenzene (BFB-used as both a tune check and surrogate compound), bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene, 1,2-dichloroethane-d4(surrogate), and toluene-d8(surrogate) at 500ug/m^3 each in humidified zero air or nitrogen. This mixture may be purchased from an approved vendor in a high-pressure cylinder at the working concentration and canisters filled directly from it for use on the sample preconcentrator. Otherwise, prepare this standard according to the procedure outlined in Volume 6.5 of the *Tekmar*-DOHRMANN Application Note.

9.2.1.1 An intermediate standard can be prepared from neat compounds in a glass static dilution bottle (SDB). After the volume of the SDB is

determined, calculate the mass of each compound to be spiked to achieve a final concentration of 5.0ug/mL. Then use the density of each neat compound to calculate the microliter amount to be spiked into the SDB. The SDB is then heated for a minimum of one hour at ~60˚C to completely volatilize all components.

Concentration of the intermediate standard prepared in a SDB is 5.0µg/mL. The amount required to achieve this concentration is determined through the use of the following equation.

$$A = \frac{(C)(V)}{D} \qquad \text{(Equation 1)}$$

Where:

A Amount of each compound required to achieve the desired concentration of the standard in the SDB (µL)
C Desired concentration of SDB (µg/mL)
V Actual volume of the SDB (mL)
D Density of the compound in question (µg/µL)

Example:

Calculate the amount of neat bromochloromethane needed to achieve the final concentration of 5.0µg/mL of that compound in the SDB.

V = 2010mL
D = 1934.4µg/µL
C = 5.0µg/mL

$$A = \frac{\left(5.0\frac{\mu g}{mL}\right)2010mL}{1934.4\frac{\mu g}{\mu L}} = 5.2\mu L$$

Table 1 – Tune, IS and Surrogate Compound Densities

Density (µg/µL)	Compound
1934.4	Bromochloromethane
1170.1	1,4-Difluorobenzene
1157	Chlorobenzene-d5
1307	1,2-Dichloroethane-d4
943	Toluene-d8
1593	BFB

9.2.1.2 The Working standard is prepared in a canister by spiking an aliquot of the stock SDB standard (8.2.1.1) using a heated gastight syringe. Connect a cleaned, evacuated canister to a source of pure diluent gas (humidified zero air) using a teflon line with a stainless steel tee directly above the canister valve. One port of the tee is fitted with a septum. Spike the SDB stock and following removal of syringe a small flow of

diluent gas to flush the spike into the can. Pressurize the can to positive 83.3 psig with humid zero air, and allow the contents to equilibrate for approximately 24 hours before using.

Concentration of the working standard prepared in a canister is 500ng/L. The final pressure of the canister is 83.3psig; therefore, the pressurized volume is 40L, which is obtained through the use of the following equation.

PV = PDF(V) (Equation 2)

Where:

PV Pressurized canister volume (L)

PDF Pressure Dilution Factor, where PF = $\frac{P_{atm} + P_f}{P_{atm} + P_i}$

P_f Final Canister Pressure

P_i Initial Canister Pressure

V Volume of canister @ 1atm

P_{atm} Atmospheric Pressure = 14.7psig

Example:

$$\frac{14.7 + 83.3}{14.7 + 0}(6L) = 40L$$

In order to prepare the canister with a concentration of 500ng/L, it must be determined how much of the intermediate standard is required. This is achieved through the use of the following equation.

$$A = \frac{(F)(V)}{(C)\left(1000\frac{ng}{\mu g}\right)} \quad \text{(Equation 3)}$$

Where:

F Desired concentration of working standard (ng/L)

V Pressurized Volume of Canister (L)

C Concentration of prepared SDB (µg/mL)

A Amount of standard (mL) of the SDB required to obtain the desired working standard concentration

Example:

$$A = \frac{500\frac{ng}{L}(40L)}{\left(5.0\frac{\mu g}{mL}\right)\left(1000\frac{ng}{\mu g}\right)} = 4mL$$

9.2.1.3 Currently the working standard is purchased in a cylinder at a certified concentration of 500ng/L (prepared by Liquid Technology Corporation). The working standard is filled directly into a canister to a pressure of 70 to 80 psig.

The internal standard (IS) cylinder typically comes from the vendor with a one year expiration date. These compounds should be stable in the high-pressure cylinder for five years or longer so the laboratory will extend the expiration date to two years from the date of preparation. The working standards are canisters filled directly from the main cylinder and are given a two month expiration when prepared in a 6L canister and a six month expiration when prepared in a 30L or greater canister. The method utilizes relative response factors for target analyte quantitation so the IS concentrations are factored out since they appear in the numerator and denominator of the final calculation.

A quantitation report with chromatogram of a TO-15 blank run will be printed as soon as a new IS cylinder is put into use and again after one year. The latter will be checked for any unexpected peaks to look for possible degradation of the IS compounds in the cylinder. These shall be kept on file with the original certificate of analysis.

9.2.2 APH Component Standard (Stock Standard) Stock standards are purchased from an approved vendor as a mixture in a balance gas of nitrogen in high-pressure inert cylinders, and are available from several vendors. Each standard cylinder must be accompanied by a certificate of analysis stating the certified concentrations of each component. These concentrations must be used as the starting point when calculating the nanogram on-column amounts for the initial calibration points. See Table 5.

9.2.3 APH Working Standards Prepare gaseous-phase APH Working Standards at a minimum of two concentration levels in 6.0L canisters pressurized with humidified zero air to 14.7psig. The contents should be allowed to equilibrate for approximately 24 hours prior to use.

Step 1: Concentration of the working standards prepared in canisters should be 200ng/L and 20ng/L. The final pressure of the canister is 14.7psig; therefore, the pressurized volume is 12L, which is obtained through the use of the following equation.

PV = PDF(V) (Equation 6)

Where:

PV Pressurized canister volume (L)

PDF Pressure Dilution Factor, where PF = $\frac{P_{atm}+P_f}{P_{atm}+P_i}$

P_f Final Canister Pressure

P_i Initial Canister Pressure

V Volume of canister @ 1atm

EXAMPLE:

$\frac{14.7+14.7}{14.7+0}(6L)$ = 12L

Step 2: Use the Entech dynamic diluter to prepare the working standards in canisters. The stock standard is typically at a concentration of 1000ng/L, so a 200ng/L can will be a 5X dilution, and the 20ng/L can will be a 50X dilution. Instructions for using the diluter and calculating flows can be found in the instruction manual and in the TO-15 SOP (VOA-TO15).

9.2.4 Initial Calibration Verification (ICV) - (Laboratory Control Sample - LCS) For the second-source standard, use the TO-15 second source working standard. This standard contains all of the target analytes and at least one calibration compound from each hydrocarbon range.

Note 2: Any of the desired standard concentrations may change as long as the equations and the appropriate densities remain the same. In addition, the SDB volumes will change with each specific SDB utilized (indicated by the etched volumes on the specific SDB being utilized). The final pressures of the canisters may also change as long as the actual pressurized volumes are properly calculated in accordance with the corresponding equations detailed in this document. Use this section to calculate the alternate concentrations, pressurized volumes of the canisters, etc., as needed.

9.3 Storage and Expiration Dates

- Static Dilution Bottle (SDB) standards (internal standard/surrogate) must be stored in an oven at a temperature of 60°C to ensure analyte vaporization. Every time a standard is prepared from the static dilution bottle (SDB), the concentration changes. To increase the useful lifetime of an SDB standard, remove volumes of 25mL or less. The volume removed can be manipulated by increasing the SDB concentration or by adjusting the canister final volume/pressure. Depending upon the volume removed, a SDB intermediate standard is stable for approximately *two months* as long as new working standards made from this standard continue to meet acceptance criteria. These bottles must be in the oven at 60°C for a minimum of one hour prior to use in preparing working standards.
- Stock Standard cylinders – These standards have an expiration date on the certificate of analysis (typically one year). Expired cylinders with sufficient volume remaining are sent back to the original vendor for recertification.
- APH Working Standards (excluding the ICV/LCS) prepared in canisters may be stored at laboratory conditions for *two months* in an atmosphere free of potential contaminants. Upon preparation, canister standards should be allowed to sit for approximately 24 hours prior to use in order for equilibration to take place. Shorter

equilibration periods may be necessary and acceptable as long as performance criteria are met.

10) Preventive Maintenance

10.1 A maintenance log will be kept documenting maintenance performed on each analytical system. The serial numbers of each instrument shall be recorded, and each log entry must include a description of the maintenance performed and be initialed by the analyst performing or observing/authorizing maintenance by an outside contractor.

The instrument maintenance log must be kept current. An entry shall be made in the appropriate log every time maintenance is performed (no matter the extent). The entry in the log must include:

(a) the date of maintenance
(b) who did the maintenance
(c) description of the maintenance
(d) proof that the maintenance activity was successful

A notation of a successful tune and continuing calibration or initial calibration and the file number that accompanies the data will serve as proof that the maintenance is complete and the instrument is in working order.

The extent of the maintenance is not important, however, it is important that a notation be included for each maintenance activity such as changing a column, tuning the instrument, changing the pump oil, cleaning the source, or ordering a part. In addition, a notation should be made in the logbook stating that no samples were analyzed during the days that the instrument was down and no active maintenance was being conducted (i.e., where no other notation was made in the logbook for those days).

10.2 Concentrating Trap Routine maintenance includes periodic solvent cleaning of the Silcosteel lines in the valve oven if contamination is suspected. Also, periodic replacement of the multi-sorbent or partial replacement of the trap if analyte specific deterioration is detected is required. After repacking the trap it should be baked for a minimum of two hours (until a clean blank is generated), whereas a partial repacking requires baking the trap for a minimum of 20 minutes (or until a clean blank is generated).

10.3 GC System Column performance is monitored by observing both peak shapes and column bleed. Over time, the column will exhibit a poor overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced (see Section 8.4). Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column.

Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column-cutting tool. When removing any major portion of the column, which will affect the retention times and elution characteristics, a change in instrument conditions may be required to facilitate nominal analytical activity.

Performance can also be due to ineffective column ferrules, which should be replaced when a tight seal around the column is no longer possible. This can be detected with the use of a leak detector.

10.4 Mass Spectrometer The Mass Selective Detector (MSD) ion source requires periodic cleaning to maintain proper performance. Symptoms of a dirty ion source include difficulty keeping the MSD in tune and fluctuating internal standard areas. The vacuum system should be serviced every six months, including changing the pump oil and checking the molecular sieve in the backstreaming trap.

10.5 Instrument Tuning The instrument is tuned with guidance from the procedure described in the Agilent Operations Manual, when necessary. The tune shall meet the tune criteria described in this document.

11) Procedure

11.1 Initial Calibration The APH Component Standards are used to calibrate the GC/MS system. Two distinct calibration operations are necessary:

Target APH Analytes: Relative Response Factors (RRFs) are calculated for the 9 Target APH Analytes (Table 4) and internal standards, based upon a correlation between the mass of analyte and area counts for the relevant quantitation ions. This allows for the individual identification and quantitation of these specific compounds. IT IS NOT NECESSARY TO DEVELOP RESPONSE FACTORS FOR ANY OTHER INDIVIDUAL APH COMPONENT STANDARD. However, an extended list of target analytes may be reported if needed since all the APH target analytes are included in the calibration for EPA Method TO-15 which is performed using the same GC and data acquisition parameters as the hydrocarbon range calibration.

Collective Aliphatic/Aromatic ranges: Relative Response Factors are calculated for C_5-C_8 Aliphatic Hydrocarbons and C_9-C_{12} Aliphatic Hydrocarbons based upon a correlation between the TOTAL mass of aliphatic APH Component Standards eluting within the range of interest and the total ion area count. A Relative Response Factor is calculated for C_9-C_{10} Aromatic Hydrocarbons based upon a correlation between the TOTAL mass of aromatic APH Component Standards eluting within this range and the total area count of extracted ions 120 and 134. Specified APH Component Standards are designated "marker" compounds to define the beginning and end of the hydrocarbon ranges.

Primary and secondary extracted ions for all APH Component Standards and recommended internal standards are provided in Table 4. The recommended internal standards and associated Target APH Analyte and Hydrocarbon Ranges are provided in Table 3.

Table 3

Internal Standards and Associated Target APH Analytes and Hydrocarbon Ranges

Bromochloromethane (IS #1)	1,4-Difluorobenzene (IS #2)	Chlorobenzene-d5 (IS #3)
1,3-Butadiene Methyl tert-Butyl Ether	Benzene Toluene C_5-C_8 Aliphatics	Ethylbenzene m&p-Xylenes o-Xylene Naphthalene C_9-C_{12} Aliphatics C_9-C_{10} Aromatics

Table 4
Primary (Quantitation) & Secondary Ions for APH Component/Internal Standards

APH Component Standard	CAS Number	Mol Wt. (g/mol)	Target APH Analyte	Quantitation Ion	Secondary Ion(s)
Bromochloromethane (IS1)	74-97-5			130	49, 130
1,3-Butadiene	106-99-	54.09	✓	54	53, 39
Isopentane (Range Marker)	78-78-4			43	42, 41, 57
Methyl-tert-butyl ether	1634-	88.15	✓	73	57, 45
n-Hexane	110-54-			57	41, 43, 56
Cyclohexane	110-82-			56	84, 41
1,4-Difluorobenzene (IS2)	540-36-			114	88
2,3-Dimethylpentane	565593			56	43, 57, 41
Benzene	71-43-2	78.11	✓	78	52, 51
n-Heptane	142-82-			43	71, 57,
Toluene	108-88-	92.14	✓	91	92, 65
Chlorobenzene-d5 (IS3)	3114-			82	117
n-Octane	111-65-			43	85, 57, 71
Ethylbenzene	100-41-	106.17	✓	91	106
2,3-Dimethylheptane	3074-			43	84,85
m-Xylene	108-38-	106.17	✓	91	106, 105
p-Xylene	106-42-	106.17	✓	91	106, 105
n-Nonane (Range Marker)	111-84-			43	57, 85
o-Xylene (Range Marker)	95-47-6	106.17	✓	91	106, 105
Isopropylbenzene	98-82-8			105	120
1-Methyl-3-ethylbenzene	620-14-			105	120
1,3,5-Trimethylbenzene	108-67-			105	120
n-Decane	124-18-			57	43, 71, 85
Butylcyclohexane	1678-			83	55, 82
p-Isopropyltoluene	99-87-6			119	105, 134
1,2,3-Trimethylbenzene	526-73-			105	120
n-Undecane	1120-			57	43, 71, 85
n-Dodecane (Range Marker)	112-40-			57	43, 71, 85
Naphthalene (Range Marker)	91-20-3	128.17	✓	128	127, 102

Table 5
Standard Concentrations of APH Component Standards for Target APH Analytes and Hydrocarbon Ranges for Initial Calibration

Range	APH Component Standards used to Establish Range Response Factor	Calib. Level	Working Std conc (ng/L)	Injection Volume	Approximate Concentration
C_5-C_8 Aliphatic Hydrocarbons	Isopentane n-Hexane Cyclohexane 2,3-Dimethylpentane n-Heptane n-Octane	1	20	25mL	0.50ng
		2	20	50mL	1.0ng
		3	20	250mL	5.0ng
		4	200	125mL	25g
		5	200	250mL	50ng
		6	200	500mL	100ng
C_9-C_{12} Aliphatic Hydrocarbons	2,3-Dimethylheptane n-Nonane n-Decane Butylcyclohexane n-Undecane n-Dodecane	1	20	25mL	0.50ng
		2	20	50mL	1.0ng
		3	20	250mL	5.0ng
		4	200	125mL	25ng
		5	200	250mL	50ng
		6	200	500mL	100ng
C_9-C_{10} Aromatic Hydrocarbons	Isopropylbenzene 1-Methyl-3-ethylbenzene 1,3,5-Trimethylbenzene 1,2,3-Trimethylbenzene p-Isopropyltoluene	1	20	25mL	0.50ng
		2	20	50mL	1.0ng
		3	20	250mL	5.0ng
		4	200	125mL	25ng
		5	200	250mL	50ng
		6	200	500mL	100ng
Target APH Analytes	1,3-Butadiene Methyl tert-Butyl Ether Benzene Toluene Ethylbenzene m,p-Xylenes[b] o-Xylene Naphthalene	1	20	25mL	0.50ng
		2	20	50mL	1.0ng
		3	20	250mL	5.0ng
		4	200	125mL	25ng
		5	200	250mL	50ng
		6	200	500mL	100ng

[a] The actual concentrations shall depend on the certified analyte concentration from the applicable manufacturer's certificate of analysis.
[b] Xylene concentration is doubled.

11.1.1 Calibration Points Analyze a minimum of five levels of the calibration standard (analyze low to high) that span the monitoring range of interest of the samples. The range is typically 0.50ng to 100ng on column (m,p-Xylene is doubled). The dynamic range is dependent on the sensitivity of a particular instrument as well as the required reporting limit for a given project and may be adjusted

accordingly. Refer to Table 5 for the approximate concentrations of the compounds of interest in the initial calibration. These concentrations may change with the purchase and/or preparation of new standards; therefore, they should be verified.

The initial calibration is performed to determine instrument sensitivity and the linearity of the GC/MS response for the target compounds. One of the calibration points from the initial calibration curve must be at the same concentration as the continuing calibration verification standard. Also, one of the standards must be at or below the method reporting limit for the compounds of interest or the MRL must be adjusted accordingly.

11.1.2 Recalibration Each GC/MS system must be recalibrated following any instrument maintenance which may change or effect the sensitivity or linearity of the instrument or if the continuing calibration verification acceptance criteria have not been met as specified in Section 12.6.4.

11.1.3 Analytical Window If time remains in the 24-hour tune window after meeting the acceptance criteria for the initial calibration, samples may be analyzed according to the procedure described in this document. If time does not remain in the analytical window, a new sequence shall commence with the analysis of the instrument performance check compound (BFB) and the continuing calibration verification standard.

11.1.4 Procedure The system should be operated using temperature and flow rate parameters equivalent to those in Section 11.5. Use the standards prepared in accordance with Section 9 of this SOP. Attach the calibration standard and internal standard canisters to the designated inlets on the preconcentrator and open the canister valves. Analyzing different volume aliquots of the calibration standards produces differing concentrations. Internal standards must be added at the same volume for every standard, sample and QC sample.

Analyte responses (target ion areas) are tabulated and recorded using the Enviroquant program. Quantitation ions for the target compounds are shown in Table 4 and the primary ion should be used unless interferences are present, in which case the secondary ion may be used.

11.1.5 Initial Calibration Requirements

Initial calibration requirements are as follows:

1. A minimum of 5 concentrations must be used to calculate the calibration curve.
2. Highest concentration, together with the lowest concentration, defines the calibration range.
3. Lowest concentration must be at or below the method reporting limit.
4. A blank should be analyzed prior to beginning the analysis of the calibration standards.
5. The initial calibration event may not be interrupted by maintenance.
6. Only one value per concentration may be used.
7. Analyze calibration standards from low to high concentration.
8. All ICAL analyses must be completed within the 24-hour tune window.
9. If 5 calibration standards are in the ICAL, one standard may be re-analyzed. If 6 to 10 calibration standards are in the ICAL, two calibration standards may be re-analyzed.
10. Point dropping policy

- Minimum of 5 consecutive concentrations must be used to calculate the calibration curve.
- Lowest concentration must be at or below the MRL and may not be dropped unless the MRL is changed to the concentration of the remaining lowest standard.
- Points at the high end may be dropped, but doing so lowers the calibration range.
- Points may not be dropped from the interior of the curve unless an assignable cause (i.e., gross dilution error, missing internal standards, purge malfunction, standard preparation error, or instrument malfunction) is accounted for and documented. In these instances, all analytes in that calibration standard must be dropped from the calibration curve as the corrective action (the reason must be documented and the results maintained with the documentation for the final ICAL).
- Dropping individual compound points from the upper or lower end of the calibration range to improve linearity is not considered an error correction. The reason for dropping these points does not need to be documented but the ICAL documentation must state the revised calibration range if the MRL must be adjusted or the calibration range is lowered for a particular compound. This must be documented on the ICAL Review Checklist.

  When an individual compound point is dropped from an ICAL both the response and concentration fields in the compound database of the method must be cleared. This ensures the average ICAL RRF calculates correctly when executing the CCV check routine.

- A calibration standard may be re-analyzed if the first analysis of the standard has been dropped and other requirements in this policy are met (i.e., still within 24 hours).
- Once the ICAL has been used to calculate and report sample results, it is not to be changed.

11.1.6 Recalibration Each GC/MS system must be recalibrated following any instrument maintenance which may change or effect the sensitivity or linearity of the instrument, if the continuing calibration verification acceptance criteria are not met and at least annually. The following procedure must be followed when updating an initial calibration method.

1. Open the most recent method.
2. Save the method with the new ICAL method ID using the "Save Method As" option. Date used in the method ID must be the date files were analyzed.
3. Quantitate midpoint standard and check retention times and integrations. Update retention times if necessary using QEdit or Easy ID (Tools → Easy ID). Requant if any changes are made and verify all peaks are identified correctly. Print.
   a. While midpoint standard is loaded update reference spectra (Continuing Calibration → Update Reference Spectra).
   b. With midpoint standard loaded update qualifier ion ratios and retention times (Initial Calibration → Update Levels → Select Update Level and then select Retention Times (Replace) and Replace Qualifier Ion Relative Responses).

c. If necessary adjust integration parameters prior to processing remaining ICAL points.

4. Quantitate remaining ICAL standards. Review each peak for retention time, integration, and print. Review low level standards for acceptable signal to noise ratios and high level standards for saturation.
5. All responses must be cleared from ICAL before updating (Initial Calibration → Clear All Calibration Responses).
6. Update responses for each standard level (Initial Calibration → Update Levels) or (Initial Calibration → Quick Levels Update). If Quick Levels Update is used do not requant datafiles.
7. Save method.
8. Check Response Factor Report and evaluate whether any points should be dropped following the criteria outlined in this SOP.
9. Save method if any changes are made.
10. Verify calibration files listed on Response Factor Report are correct.
11. Verify file ID, acquisition time, quant time, update time, and last update information is correct on the Calibration Status Report.

11.1.7 Initial Calibration Review Analyst's calculation and assessment along with a peer review of all ICAL data and documentation as stated in Attachment 2 is required before the ICAL may be used to analyze samples. In the case where samples are placed on the autosampler and allowed to run overnight, the sample results may only be reported if the ICAL is reviewed and found to be acceptable. The ICAL checklist in Attachment 2 must be used to document the review and approval process.

Analyte concentrations, which are not "real", not to be reported, or otherwise marked off the initial calibration, should be followed by a short explanation regarding the reason for the omission.

11.1.8 Initial Calibration File An ICAL file is to be created for each initial calibration performed per instrument into which is placed the following ICAL documents. The file shall remain in the laboratory and be filed by instrument and date.

- ICAL Checklist filled out, reviewed and approved
- BFB tune analysis report
- Blank analysis quantitation report
- Calibration status report (aka Calibration History)
- Relative Response Factor Report / Percent Relative Standard Deviation
- Quantitation report for each calibration standard (including manual integration documentation – before and after manual integration)
- ICV quantitation report and %recovery report.

11.2 Initial Calibration Verification Standard Verify the initial calibration by analyzing an initial calibration verification standard (ICV). This standard shall be obtained or prepared from materials acquired from a different manufacturer or lot from that of the initial calibration and prepared according to Section 9.2.4. At a minimum, it must contain 1,3-butadiene, benzene, toluene, ethylbenzene, m-&p-xylene, o-xylene, and naphthalene, and at least one compound from each hydrocarbon range. Methyl tert-butyl ether may be included but may have wider recovery acceptance limits.

Inject 25ng or less (refer to the appropriate manufacturer's certificate of analysis for the actual secondary source standard concentrations) of the ICV standard depending on the dynamic range of a given instrument.

11.3 Sample Preparation and Leak Check The initial pressure/vacuum is checked and the canister pressurized as needed upon receipt by the laboratory. Samples collected in canisters shall be pressurized with humidified zero grade air or Nitrogen. However, if the samples are to be analyzed in accordance with EPA Method 3C then the samples must be pressurized with UHP Helium. The client must be made aware of this in advance and given the option of either submitting two canisters for analysis or receiving a report with qualified results.

Canister Pressurization Samples must be pressurized (to approximately 3.5psig) prior to analysis with humidified zero air (refer to exception stated above). This may be accomplished by connecting the sample canister to a source of pure diluent gas (zero air) using a teflon line with a stainless steel tee directly above the canister valve. One port of the tee is fitted with a septum and injecting 100uL of water into the can through the septum and allowed to vaporize for approximately 10 minutes. Alternatively, pressurize at a fill station by bubbling the diluent gas through a zero air bubbler. Both of these procedures shall utilize ASTM Type II water or equivalent. Additional information may be found in the *Standard Operating Procedure for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters*. Initial and final pressures shall be recorded and the dilution factor created by filling the sample canister is calculated using Equation 25 in Section 13.3.4.

Leak Check Connect the canister(s) to the autosampler. Place a ¼" stainless steel nut and ferrule on the inlet line facing the canister. Push the inlet line into the orifice of the canister and hold in place while tightening the fitting finger tight. Turn the stainless steel nut ¼ turn more with a wrench. The canister valves should be closed at this point. For Bottle Vacs, connect the female Micro-QT fitting to the autosampler. A leak check must be performed before connecting the sample bottles since the valve is open as soon as the bottle is connected.

Leak Checks – Leak check all canister inlet connections. Analysis may not begin until the leak check has passed for each canister being tested. If a leak is detected, it should be confirmed by placing on a different location. In addition, the valve threads should be inspected for defects which may prevent a good seal with the AutoCAN. Once a canister has "failed" the leak check it must be tagged, an NCAR initiated, and the PM notified. Regardless of what the client or PM specifies as the fate of the sample, the canister must be put on maintenance hold to complete a full 24-hour leak check. A yellow sheet is to be completed in addition to, but not in lieu of an NCAR. This is a fixed QA procedure with no allowance for deviation.

11.4 Analytical Sequence and Data System Setup

11.4.1 Data System

For the Tekmar AutoCan, fill in the sequence log of the Teklink program with the appropriate information. Refer to the Section 11.5.1 for the operating parameters.

For the HP Chemstation, load the appropriate acquisition method for the GC/MS in the top window of the Chemstation program. Suggested GC/MS operating parameters are given in Section 11.5.2.

11.4.2 Analytical Sequence For this internal standard calibration method analysis, a CCV standard is to be analyzed every 24 hours. That is, the last analysis in the sequence must be started within 24 hours from the time of the initiation of the sequence. The initiation is considered to be the injection of the BFB tune

standard.

The analytical sequence must be completed for the analysis of ≤20 field samples. A method blank (MB) shall be run to monitor for laboratory introduced contamination. There must be at a minimum a laboratory duplicate (LD) analyzed in each batch to access batch precision. A laboratory control sample (LCS) shall be analyzed at a rate of at least one per batch of twenty or fewer samples. The concentration of the LCS (ICV standard) should be at the lower end of the calibration curve as an indication that the system allows for good recovery at those concentrations. The following is the analytical sequence guideline for this method.

Analytical Sequence Guideline

With Calibration	Tune Check[1]
	Calibration Standards (5 Standards Minimum)
	ICV Standard[2] (Acts as the ICV and LCS)
	QC Canister Checks[6]
	MB[7]
	Sample(s)
	Laboratory Duplicate[4]
With Continuing	CalibrationTune Check[1]
	CCV Standard[5]
	QC Canister Checks[6]
	MB[7]
	LCS[3]
	Sample(s)
	Laboratory Duplicate[4]

[1] The introduction of the tune check standard is the start of the 24 hour analysis window. The instrument performance check solution must be analyzed initially and once per 24 hour time period of operation.
[2] In this scenario, the ICV may also be evaluated as the LCS.
[3] An LCS shall be analyzed at a rate of 1 in 20 or fewer samples. The LCS is the second source calibration check standard.
[4] A laboratory duplicate must be analyzed at a rate of 1 per 20 or fewer samples. The duplicate must be reported even if it is a batch duplicate.
[5] A CCV must be analyzed at the beginning of every analytical sequence.
[6] Any number of QC check canisters may be analyzed in the sequence to determine a canister cleaning batch or batches acceptability.
[7] Any of the QC Check Canisters may serve as the method blank as long as the minimum requirements detailed in this document are met. A method blank shall be analyzed at a rate of 1 in 20 or fewer samples.

11.5 Conditions

11.5.1 Sample Collection Conditions The suggested settings and system parameters are as follows:

Adsorbent Trap

Set Point:	40˚
Sample Volume:	25ml to 1,000ml
Dry Purge:	300mL
Sampling Rate:	100ml/min or 40ml/min
Desorb Temp.:	210˚C
Desorb Flow Rate:	8-10mL/min He
Desorb Time:	3.0 minutes

Refocusing Trap

Temperature:	-175˚C
Injection Temp.:	150˚C
Injection Time:	1.0 min

Adsorbent Trap Reconditioning Conditions

Temperature:	10°C above desorb temperature
Initial Bakeout:	2 hours or until clean blank is obtained
After each run:	10 minutes

11.5.2 GC/MS System

Optimize GC conditions for compound separation and sensitivity.

Item	Condition
Carrier Gas	Helium
Flow Rate	1.0-1.6mL/minute
Temperature Program	Initial Temperature: 10˚C Initial Hold Temperature: 1 minute Ramp Rate: 5˚C/min to 50˚C 2nd Ramp: 10˚C/min to 100˚C 3rd Ramp: 20˚C/min to 240˚C for 4 min hold
Detector B (MSD *Interface)*:	260˚C
Electron Energy	70 Volts (nominal)
Mass Range	33 to 280 amu (SCAN mode)
Scan Time	To give at least 10 scans per peak, not to exceed 1 second per scan.

11.6 Retention Time Windows The laboratory should calculate retention time windows initially and whenever a new GC column is installed. The laboratory must retain these data.

Before establishing retention time windows, ensure that the GC/MS system is operating within optimum conditions. Analyze an APH Calibration Standard on three separate occasions throughout the course of a 72-hr period. Serial analyses over less than a 72-hr period may result in retention time windows that are too restrictive.

Calculate the standard deviation of the three absolute retention times for each Target APH Analyte, range "marker" compound, internal standard, and MS tuning standard.

The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each analyte of interest. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

In those cases where the standard deviation for a particular standard approaches zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop an operational retention time window.

Table 2
APH Range "Marker" Compounds and Range Retention Time Windows

Hydrocarbon Range	Beginning Marker	Ending Marker
C_5-C_8 Aliphatic	0.1 min. before isopentane	0.01 min. before n-nonane
C_9-C_{12} Aliphatic Hydrocarbons	0.01 min. before n-nonane	0.1 min. after naphthalene*
C_9-C_{10} Aromatic Hydrocarbons	0.1 min. after o-xylene	0.1 min before naphthalene

*The method specifies using n-dodecane as this marker, but in practice naphthalene elutes after n-dodecane so the laboratory must use naphthalene as the marker.

The relative retention time (RRT) and RRT window for each Target APH Analyte, internal standard, and hydrocarbon range "marker" compound must be verified on a daily basis. The RRT for each analyte of interest shall be established as the midpoint of the window. The retention time window equals the midpoint ± three times the standard deviation (Equation 9).

11.7 Instrument Performance Check Since the BFB tuning compound is included in the internal standard canister and a autosampler is used, it is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to the reduction and approval of any data collection. The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or continuing calibration verification criteria) begins at the injection of the BFB, which shall be documented in laboratory records. Upon completion of the successful BFB tune, the tune report must be printed and retained on file for future reference.

The following is the procedure to follow when performing the instrument performance check.

- Inject 50ng or less (on column)
- Three scans (peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.
- Background subtraction is conducted using a single scan prior to the elution of BFB.

All subsequent standards, samples and QC samples associated with a BFB analysis must use identical instrument conditions. Refer to Section 12.6.1 (Table 7) for the acceptance criteria and required corrective action.

11.8 Continuing Calibration Verification Standard Verify the calibration each working day, where necessary (e.g., an ICAL was not analyzed or the 24-hour tune window has closed) by analyzing a continuing calibration verification (CCV) standard from the initial

calibration standard canister. The concentration of the calibration verification should be varied within the established calibration range.

11.9 Canister Quality Control Check and Method Blank A Quality Control (QC) check canister may also serve as a method blank (see note 1 below) as long as the analyte concentration requirements stated in the canister quality control check section (Section 11.9.1) and the other requirements (refer to Section 12.6.7 for internal standard requirements) are met. If a QC canister fails with respect to the analyte concentration criterion, it may still be used as a method blank as long as the method blank criteria stated in 12.7.2 are met. If a QC canister still fails, another QC canister or a new canister must be prepared and analyzed (per Section 11.9.2) in order to verify that no system contamination exists.

Note 1:The use of a QC canister as a method blank is considered acceptable since a canister that has been sent into the field, returned and cleaned more closely resembles the manner in which client samples are handled.

11.9.1 Canister Quality Control Check The actual cleaning procedure, number of cans to select for analysis (to release a cleaning batch) and corrective actions are covered in the *Standard Operating Procedure for Cleaning and Certification of Summa Canister and Other Specially Prepared Containers* and are not covered in this section. However, the procedure for analyzing and certifying a cleaning batch is included.

The canister to be checked, shall be pressurized with humidified zero grade air prior to analysis. Analyze an aliquot of one liter along with the same volume of internal standard as standards and samples. The unique laboratory barcode given to a canister shall be the information included in the sample analysis identification, which is for tracking purposes. A canister is considered "clean" if the analysis shows <0.2ppbv of any target analyte or hydrocarbon range (refer to Note 1).

11.9.2 Method Blank In order for a method blank to be considered acceptable all target analytes must be less than the method reporting limit and fulfill the additional requirement in Section 12.6.5. If the QC canister(s) fail the corresponding criteria then the following must be performed.

- Prepare a canister that has not left the building by pressurizing with humidified zero air.
- Analyze an aliquot of the blank (1 liter) with internal standard
- Be consistent with the volume of internal standards introduced for each analysis.

Additionally, analyze a method blank whenever a high concentration sample is encountered and carryover is suspected.

The analyst should cross out those concentrations that are not real and initial and date the quantitation report for those QC Check canisters and method blanks that meet the acceptance criteria included in this section.

11.10 Laboratory Control Sample The laboratory control sample is an injection of the initial calibration verification standard. Inject the LCS (ICV) at concentrations at or below the midpoint of the calibration curve. Make sure that all of the pertinent information is included on the quantitation report including the sample identification (LCS), concentration, standard used, and analyst.

11.11 Sample Analysis Prior to analysis, all sample containers should be at temperature equilibrium with the laboratory.

- Attach sample canisters Tekmar AUTOCan using a 9/16" wrench. Bottle Vacs use a proprietary quick connect fitting (Micro-QT, Entech Instruments).
- Before opening the valve, check for leaking fittings by running the leak check program in the Teklink software. Quick connect fittings must be leak checked before connecting the sample container.
- If system is leak tight, open the canister valves and start the automated preconcentration procedure. Make sure the Chemstation data acquisition software has been readied.
- Maintain the trap at an elevated temperature until the beginning of the next analysis.
- Introduce the same volume of internal standards as used for the standards and QC samples.

Note 1: The secondary ion quantitation is only allowed if there is sample matrix interference with the primary ion. If the secondary ion quantitation is performed, document the reasons in the instrument run logbook and/or on the quantitation report (initial and date any notation).

Note 2: Each female Micro-QT fitting must be purged after use to remove any remaining sample residue and prevent contamination from subsequent usage. Connect a male Micro-QT fitting to a source of ultrapure or carbon-filtered gas. Adjust the pressure to about 10 psig using an inline regulator. Connect the female fitting for several seconds, then remove and place in an oven kept at 60ºC until the next use. Do not heat the fitting higher than 80ºC.

11.11.1 Qualitative Identifications The Target APH Analytes must be identified by an analyst competent in the interpretation of chromatograms and mass spectra. Two criteria must be satisfied to verify the identification: (1) elution of the component in the sample at the same GC relative retention time (RRT) as the component in the standard, and (2) agreement of the sample component and standard component mass spectra.

If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned using extracted ion current profiles for the ion unique to the component of interest.

For comparison of the standard and sample component mass spectra, mass spectra of standards obtained on the GC/MS under the same instrument conditions are required. Once obtained, these standard spectra may be used for identification and reference purposes. The requirements for qualitative verification by comparison of mass spectra are as follows:

All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

The relative intensities of ions specified must agree within ±20% between the standard and sample spectra.

Ions greater than 10% in the sample spectrum must be considered and accounted for by the analyst making the comparison.

The primary and secondary ions for all APH Component Standards are provided

in Table 4.

11.11.2 Sample Dilution If any target analyte results are above the highest level of the initial calibration, a smaller sample aliquot should be analyzed. The smallest volume used shall not be less than that used for the initial calibration (see Table 5). The dynamic range of volume aliquots for the automatic cryogenic concentrator is 15ml to 1L. If a volume smaller than 15ml is to be analyzed, a dilution should be made in a Tedlar bag, or the sample directly injected using a gastight syringe. Guidance in performing dilutions and exceptions to this requirement are given below.

- Use results of the original analysis to determine the approximate dilution factor required and get the largest analyte peak within the initial calibration range.
- The dilution factor chosen should keep the response of the analyte peak for a reported target compound in the upper half of the initial calibration range of the instrument.
- All dilution factors (Equation 25) must be documented and included in the final report.

Note: Refer to Section 16.7.3 for requirements on reporting results outside of the initial calibration range.

11.12 Manual Integration The integration for each peak shall be checked to ensure that it has been integrated properly. Assuming an incorrect automatic integration the analyst shall conduct the manual integration in accordance with the *SOP for Manual Integration Policy* including all documentation and reviews associated with the process. The review shall include the analyst and reviewer initialing and dating the manual integration as an indication of acceptability and approval.

12) Quality Control Requirements and Corrective Action

12.1 This section of the standard operating procedure contains technical acceptance criteria. To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.2 Any maintenance which may alter instrument sensitivity or linearity must result in the re-analysis of the entire sequence including the tune compound, ICAL or CCV. Corrective actions shall follow the procedures outlined in the *SOP for Nonconformance and Corrective Action,* where appropriate.

12.3 Analytical Sequence Refer to Section 11.4.1 for the analytical sequence requirements. All analytical sequences and data must be recorded in an instrument run logbook.

12.4 Minimum Instrument QC (Additional) The following are additional requirements or are reiterated from previous sections.

- Internal standards used must be adequately resolved from individual compounds in the APH Component Standard.
- Retention time windows and relative retention times must be established for each target APH analyte, range "marker" compound, and internal standard initially and each time a new GC column is installed, and must be verified and/or adjusted on a daily basis (see Section 12.6.4).

12.5 Initial and Periodic Method QC Demonstrations The following procedures must be conducted as an initial demonstration of laboratory capability (IDLC). Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method or operational problems.

12.5.1 Accuracy and Precision To demonstrate initial laboratory capability, analyze a minimum of four replicate samples obtained from a humidified canister fortified with each Target APH Analyte.

- Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as a percentage of true value) for each analyte and hydrocarbon range, and the replicate precision (as %RSD) of the measurements for each analyte.
- For each analyte and hydrocarbon range, the mean accuracy, expressed as a percentage of the true value, must be between 70% and 130%, and the %RSD must be less than or equal to 25. The IDLC must meet these conditions for analysis to proceed.
- If desired, the accuracy and precision evaluation may be combined with the MDL evaluation specified in Sections 12.5.2 and 12.5.3.

12.5.2 Method Detection Limits for Target APH Analytes Although the method does not require that MDL studies be performed, the APH target compounds are a subset of the EPA TO-15 analysis for which laboratory performs annual MDL determinations as follows. Analyze a minimum of seven replicate samples obtained from a canister fortified with all Target APH Analytes of interest at 3 to 5 times the calculated or estimated Instrument Detection Limits (IDLs) or at the low level initial calibration standard concentration. Analyze each replicate according to the procedure described in this document. Calculate the Method Detection Limit (MDL) of each analyte using Equations 9 and 10 and Table 6 below.

Additionally, process a minimum of seven method blank samples according to the procedure described in this document. Refer to the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* for the method blank MDL calculation and additional requirements for establishing the MDL.

Equation 9: Standard Deviation

$$SD = \sqrt{\sum_{i=1}^{N} \frac{\left(C_i - \overline{C}\right)^2}{N-1}}$$

where:

C_i are the individual concentrations from each MDL replicate analysis

$\overline{C}$ Average (or Mean) concentration of all MDL replicate analyses

N total number of MDL replicate analyses

Equation 10: Method Detection Limit

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level.
SD = standard deviation of the replicate analysis.

Table 6
Student t Values

Number of replicates	t value
7	3.143
8	2.998
9	2.896
10	2.821

12.5.3 Method Detection Limits for Hydrocarbon Ranges The method does not require that MDL studies be performed. However, the laboratory may choose to perform them in anticipation of client requests. Analyze a minimum of seven replicate samples obtained from a humidified canister fortified with all of the APH range calibration compounds at 3 to 5 times the calculated or estimated Instrument Detection Limit (IDL) or at the low level initial calibration standard concentration. Analyze each replicate according to the procedures described in this document. Calculate the Method Detection Limit (MDL) of each range using Equations 9 and 10 and Table 6.

Additionally, process a minimum of seven method blank samples according to the procedure described in this document. Refer to the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* for the method blank MDL calculation and additional requirements for establishing the MDL.

12.5.4 Method Reporting Limits

12.5.4.1 Target APH Analytes The method reporting limit for each target APH analyte must be at or above the low level calibration standard and should be verified on an annual basis by analyzing at least 4 replicate samples from a canister spiked at the reporting limit, where the precision is demonstrated to be equal to or less than 25% RSD, and the mean accuracy is demonstrated to be between 70%-130% of the spiked value.

12.5.4.2 Collective Hydrocarbon Ranges The method recommends that the MRL for each hydrocarbon range be based upon the concentration of the lowest range calibration standard for the components that make up this range. The minimum MRL for each range is equal to the sum of the mass amounts of all the individual components in the lowest calibration standard point that are used for creating that range's RRF. In practice, this leads to MRLs that are so low that chromatographic baseline noise often yields a false positive result. The laboratory will

set the MRLs at or above this level so long as it meets the data quality objectives of the data user.

12.6 Ongoing Method QC Demonstrations

12.6.1 Instrument Performance Check

Acceptance Criteria – The GC/MS system must meet the mass spectra ion abundance criteria listed in Table 7. The appropriate corrective action is described below. Results of the BFB tune check as well as any actual tuning must be recorded and a copy of the tune report maintained on file.

Table 7 BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	8.0 – 40.0 percent of the base peak
75	30.0 – 66.0 percent of the base peak
95	base peak, 100 percent relative abundance
96	5.0 – 9.0 percent of the base peak
173	less than 2.0 percent of mass 174
174	50.0 to 120.0 percent of the base peak
175	4.0 – 9.0 percent of mass 174
176	greater than 93.0 percent but less than 101.0 percent of mass 174
177	5.0 – 9.0 percent of mass 176

Corrective Action – Re-analyze the BFB compound or perform auto tune or manual tune and then re-analyze BFB. If the BFB acceptance criteria are still not met, the MS must be retuned according to the procedure outlined in the instrument user's manual. Perform necessary maintenance and make notations in the instrument maintenance logbook. It may be necessary to clean the ion source, or quadrupole, or take other necessary actions to achieve the acceptance criteria.

12.6.2 Initial Instrument Calibration

Acceptance Criteria

- Refer to Section 11.1.5 for the initial calibration procedure requirements (i.e., number of points, dropping points, etc.)
- The calculated percent relative standard deviation (%RSD, linear or quadratic regression is not allowed) for the relative response factors (RRF) for each compound in the calibration standard must be ≤30% with *Naphthalene* up to ≤40%.
- All of the following information must be retained to permit reconstruction of the initial instrument calibration: calibration date, test method, instrument, analysis date, analyte identification, analyst's initials, concentration and responses, and response factors.
- All initial instrument calibrations must be verified with an acceptable initial calibration verification (ICV) (refer to Section 12.6.3).

Corrective Action – Follow the initial calibration guidelines detailed in this document for information on re-analyzing or dropping points and the restriction of maintenance performed during the analysis of the initial calibration standards. If the criteria are not met it may be necessary to perform maintenance, if this is the case then all calibration points must be re-analyzed.

12.6.3 Initial Calibration Verification Standard (ICV) / Laboratory Control Sample (LCS)

Acceptance Criteria – The spike recovery (%R) must be between 70%-130%.

Corrective Action – If the technical acceptance criteria are not met, reanalyze and if it still fails prepare a new canister and analyze. If the criteria are still not met inspect the system for possible sources and perform any necessary maintenance and make a notation in the maintenance logbook of any steps taken. It may be necessary to clean the ion source or change the column. Perform a new initial calibration if any performed maintenance has altered instrument linearity and/or sensitivity. A demonstration of an acceptable ICV is required.

12.6.4 Continuing Calibration Verification (CCV)

Acceptance Criteria

- The percent difference (%D) must be ≤30% (single analyte or hydrocarbon range). If more than one compound fails to meet this criteria, or any one analyte or range is >50% then the CCV is considered unacceptable.
- The relative retention time (RRT) and RRT window for each target APH analyte, internal standard, and hydrocarbon range "marker" compound must be verified with each CCV analyzed.

Corrective Action – If the continuing calibration verification technical acceptance criteria are not met, reanalyze and if it still fails prepare a new canister and analyze. If the criteria are still not met inspect the system for possible sources of the problem and perform any necessary maintenance and make a notation in the maintenance logbook of any steps taken. It may be necessary to clean the ion source or change the column.

If any corrective action and/or reanalysis fails to produce continuing calibration verification within acceptance criteria (analyzed immediately following the initial failure), then either two consecutive successful verifications must be performed following corrective action or a new initial calibration must be performed. However, sample data associated with an unacceptable calibration verification may be reported as qualified data under the following special conditions:

When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported. If however, the acceptance criteria for the continuing calibration verification are exceeded low, i.e., low bias, and there are associated samples that are non-detects, then those non-detects may be reported with the reporting limit adjusted to the next level in the calibration curve (typically 5 times higher) to prove the nonexistence of a false negative. Otherwise the sample affected by the unacceptable CCV shall be reanalyzed after a new calibration curve has been established, evaluated and accepted.

12.6.5 Method Blank

Acceptance Criteria – The method blank result for any target analyte must not be greater than the reporting limit and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.

Corrective Action – If the analyte concentration results in the blank do not meet the acceptance criteria repeat analysis with remaining QC canisters until results are acceptable.

If the analyte results in the blank still do not meet the acceptance criteria the source of the problem must be investigated and measures taken to eliminate the source. Determine whether the contamination is from the instrument or due to contamination in the blank container (if results from the new can are not acceptable then the system is probably contaminated). Regardless, appropriate corrective measures must be taken and documented before sample analysis proceeds. However, if this is not a possibility and the results must be reported follow the reporting requirements stated in Section 16.3.

12.6.6 Laboratory (Sample) Duplicate

Acceptance Criteria – The relative percent difference (RPD) must be <30% when the results are >5x the MRL.

- If the RPD exceeds 30 and both results are >5x the MRL, the sample analysis must be repeated.
- If an analyte is detected in one analysis at >5x the MRL but not detected in the duplicate analysis, the analysis must be repeated.
- If an analyte is detected in one analysis at ≤5x the MRL but not detected in the duplicate analysis, the RPD is not calculable and the analysis does not have to be repeated.

Corrective Action – If the duplicate results do not meet the technical acceptance criteria, perform another duplicate analysis. If the results are still unacceptable and the associated samples are not reanalyzed then all of the sample results in the associated batch must be flagged accordingly.

12.6.7 Internal Standards

Acceptance Criteria – Internal standards must be adequately resolved from individual compounds in the APH calibration standard. A minimum separation requirement of 50% (maximum peak height to valley height) must be met, particularly for n-hexane and bromochloromethane (IS1). The internal standard area counts of each sample, blank, and Laboratory Control Sample must be evaluated against the corresponding continuing calibration standard or the midlevel initial calibration standard (if analyzed in the same sequence). The internal standard area counts must be within 50-200% of the continuing calibration standard area counts. If the internal standards fall outside this range, the sample, blank, or Laboratory Control Spike must be reanalyzed.

Corrective Action – If the problem is with the instrument, perform maintenance. If the problem is with a sample, check for interferences. If the response is high, it is likely that interference is present. In this case, lower the volume or aliquot of the sample and re-analyze. If the problem persists, report the results with the best quality and qualify the results. If the problem is corrected with the lower volume analysis, report those results.

12.6.8 Sample Analysis

Acceptance Criteria – Sample results must be quantitated from the initial instrument calibration and may not be quantitated from any continuing

instrument calibration verification.

- The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, initial calibration verification technical acceptance criteria.
- All target analyte peaks must be within the initial calibration range or reported with the appropriate data qualifier.
- The internal standard with each sample must comply with the requirements listed in Section 12.6.7.
- Each analyte, in order to be reported, must meet the qualitative identification requirements listed in Section 11.11.1.

Corrective Action – When corrective actions are made, samples analyzed while the instrument was not functioning properly must be re-analyzed or the appropriate data qualifiers must be attached to the results.

To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.7 Sample's Holding Time Expired The customer is to be notified that the sample's holding time was missed and the customer is to decide if the sample analysis is to continue. The documentation of missed holding time and the client's decision to proceed must be included in the corresponding job file. A statement dictating all holding time occurrences must accompany the sample results in the final report.

13) Data Reduction and Reporting

13.1 Initial Calibration Calculations

13.1.1 Target APH Analytes Quantitation of the target analytes is done using the same data analysis method used for EPA TO-15 since all the APH target analytes are part of the laboratory's TO-15 analyte list. Tabulate the area response of the characteristic ions against the mass of each Target APH Analyte and internal standard and calculate relative response factors (RRFs) for each compound using Equation 12. Perform this calculation for each Target APH Analyte.

Equation 12: Relative Response Factor for Target APH Analytes

$$RRF = [(A_{EC}) * (C_I)] / [(A_{EI}) * (C_C)]$$

where:

RRF = relative response factor
A_{EC} = area count of the extracted ion for the analyte of interest
C_I = mass of internal standard (ng)
A_{EI} = area count of the extracted ion for the associated internal standard
C_C = mass of analyte of interest (ng)

13.1.2 Hydrocarbon Ranges

13.1.2.1 Calculate a response factor for the C_5-C_8 Aliphatic Hydrocarbon range using the following steps.

Using total ion integration, sum the individual peak areas of the six (6) APH Component Standards that are used to establish an average range response factor for C_5-C_8 Aliphatic Hydrocarbons, as designated in Table 5. Do not include the peak areas of internal/tuning standards.

Using the total area generated, calculate the Range RRF using Equation 13.

Equation 13: Relative Response Factor for C_5-C_8 Aliphatic Hydrocarbons

$$\text{Range } RRF = [(A_T)*(C_I)] / [(A_{EI2})*(C_T)]$$

Where:

Range RRF = relative response factor for the hydrocarbon range
A_T = total ion area count of the six aliphatic APH Component Standards which elute within this range (see Table 5)
C_I = mass of internal standard #2, ng (1,4-Difluorobenzene)
A_{EI2} = area count of the extracted ion for internal standard #2
C_T = summation of the masses of the six aliphatic APH Component Standards (ng) which elute within this range (see Table 5)

13.1.2.2 Calculate a response factor for the C_9-C_{12} Aliphatic Hydrocarbon range using the following steps.

Using total ion integration, sum the individual peak areas of the six (6) APH Component Standards that are used to establish an average range response factor for C_9-C_{12} Aliphatic Hydrocarbons, as designated in Table 5. Do not include the peak areas of internal/tuning standards.

Using the total area generated, calculate the Range RRF using Equation 14.

Equation 14: Relative Response Factor for C_9-C_{12} Aliphatic Hydrocarbons

$$\text{Range } RRF = [(A_T)*(C_I)] / [(A_{EI3})*(C_T)]$$

where:

Range RRF = relative response factor for the hydrocarbon range
A_T = total ion area count of the six aliphatic APH Component Standards which elute within this range (see Table 5)
C_I = mass of internal standard #3, ng (Chlorobenzene d5)
A_{EI3} = area count of the extracted ion for internal standard #3
C_T = summation of the masses of the six aliphatic APH Component Standards (ng) which elute within this range.

13.1.2.3 Calculate a response factor for the C_9-C_{10} Aromatic Hydrocarbon range using the following steps.

Using extracted ion 120, sum the individual peak areas of the five (5) APH Component Standards that are used to establish an average range response factor for C_9-C_{10} Aromatic Hydrocarbons (only four of the compounds will contribute area from m/z 120), as designated in Table 5. Do not include the peak areas of internal/tuning standards.

Using extracted ion 134, sum the peak areas of the five (5) APH Component Standards that are used to establish an average range response factor for C_9-C_{10} Aromatic Hydrocarbons (only one compound will contribute area from m/z 134), as designated in Table 5. Do not include the peak areas of internal/tuning standards.

Sum the area counts from each extracted ion.

Using the area count generated, calculate the RRF using Equation 15.

Equation 15: Relative Response Factor for C_9-C_{10} Aromatic Hydrocarbons

$$\text{Range } RRF = [(A_T)*(C_I)] / [(A_{EI3})*(C_T)]$$

where:

Range RRF = relative response factor for the hydrocarbon range
A_T = summation of area counts using extracted ions 120 and 134
C_I = mass of internal standard #3, ng (Chlorobenzene d5)
A_{EI3} = area count of the extracted ion for internal standard #3
C_T = summation of the masses of the five aromatic APH Component Standards (ng) which elute within this range (see Table 5)

Calculate the average response factor for each of the Target APH Analytes and each hydrocarbon range.

Calculate the percent relative standard deviation (%RSD) of the response factors over the working range of the curve for each of the Target APH Analytes and each hydrocarbon range using Equation 16.

Equation 16: Percent Relative Standard Deviation

This equation is also used for initial demonstration of capabilities, method detection limits studies, and method reporting limit verifications.

$$\%RSD = [(SD_{n-1}) / (AVG_X)]*100]$$

where:

%RSD = percent relative standard deviation
SD_{n-1} = standard deviation (n-1 degrees of freedom)
AVG_x = average response factor from the initial calibration curve

13.2 Sample Calculations

13.2.1 Individual Target APH Analytes The average response factor from the initial calibration is used to calculate the amount of analyte detected in the sample.

Equation 17 is used to calculate the mass of sample analyte in ng. Equation 18 is used to convert ng to µg/m³. Equation 19 is used to convert of µg/m³ to ppbV.

Equation 17: Calculation of Analysis Results in ng

$$ng = [(A_x)*(C_{IS})] / [(A_{IS})*(RRF_{avg})]$$

where:

A_x = area of quantitation ion for the Target APH Analyte (see Table 4)
C_{IS} = mass of the internal standard
A_{IS} = area of quantitation ion for the associated internal std (see Table 4)
RRF_{avg} = average response factor for the specific compound to be measured**

Equation 18: Conversion of ng to µg/m³

$$\mu g / m3 = (ng / VA) * DF$$

where:

V_A = volume of sample analyzed (liters)
DF = dilution factor (Equation 25); if no dilution was made, the dilution factor =1

Equation 19: Conversion of µg/m³ to ppbV

$$ppbV = (\mu g / m3) * 24.46 / MW$$

where:

MW = molecular weight of the compound of interest, g/mol (see Table 4 for a list of the molecular weights of the Target APH Analytes)

13.2.2 Hydrocarbon Ranges The average range response factor from the initial calibration is used to calculate the mass (ng) of range hydrocarbons in samples. Collective peak area integration for the hydrocarbon ranges must be from baseline to baseline (i.e., must include the unresolved complex mixture).

13.2.3 The contribution of compounds not meeting the definition of aromatic or aliphatic hydrocarbons may be omitted from the collective hydrocarbon range calculations at the discretion of the laboratory and the data user. Only peaks with a peak height greater than half of the nearest internal standard need to be evaluated for exclusion. The guidance for making this decision includes the following:

- If the non-APH compound co-elutes with an aliphatic petroleum hydrocarbon, the area may not be subtracted from the aliphatic range.
- In complex sample matrices (i.e. many co-eluting peaks, complex petroleum patterns), this type of data adjustment may not be possible.
- Spectral identification of the excluded peak must be evaluated by a qualified mass spectrometrist. The analyst should consider the quality of the spectral library match, presence and relative intensity of major ions, and potential interferences in making a professional judgment on exclusion.

C_5-C_8 Aliphatic Hydrocarbons

- Using total ion integration, sum all peaks in the appropriate retention time window as specified in Sections 11.6 and Table 2.
- From this sum, subtract the total ion area counts of all internal standards and surrogates which elute in this range (all three of the recommended internal standards and two of the surrogates elute in this range). Also subtract the total ion area counts of all non-APH compounds that are not to be included in the final result.
- Calculate a preliminary mass amount in ng using Equation 20.

  Equation 20: Calculation of Preliminary Sample Analysis Results (ng)

  $$ng = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})]$$

  where:

  A_x = total ion area count of all peaks eluting within C5-C8 Aliphatic Hydrocarbon range window
  C_{IS} = mass of the internal standard, ng
  A_{IS} = area of quantitation ion for internal standard #2 (1,4-Difluorobenzene)
  RRF_{avg} = average range response factor for the C5-C8 Aliphatic Hydrocarbon range

- From the preliminary amount (ng), calculate an adjusted mass amount of range hydrocarbons by subtracting the masses of Target APH Analytes which elute in this range (MtBE, benzene, toluene, ethylbenzene, m-xylene, p-xylene, and o-xylene,).
- Convert the adjusted ng value to µg/m³ using Equation 21.

  Equation 21: Conversion of ng to µg/m³

  $$\mu g / m^3 = (C_{ng} / V_A) * DF$$

  where:

  C_{ng} = adjusted total mass of range hydrocarbons in ng
  V_A = volume of sample analyzed (liters)
  DF = dilution factor (Equation 25); if no dilution was made, the dilution factor = 1.

<u>C_9-C_{10} Aromatic Hydrocarbons</u>

- Using extracted ion 120, sum all peaks in the appropriate retention time window as specified in Section 11.6 and Table 2.
- Using extracted ion 134, sum all peaks in the appropriate retention time window as determined in Section 11.6 and Table 2.
- Sum the areas of ions 120 and 134.
- Subtract the extracted ion area (mass 120 and 134) of any non-APH compounds that are not to be included in the final result.
- Calculate an amount in ng using Equation 20, using the summed areas of ions 120 and 134.
- Convert the ng value to µg/m³ using Equation 21.

<u>C_9-C_{12} Aliphatic Hydrocarbons</u>

- Using total ion integration, sum all peaks in the appropriate retention

time window as specified in Section 11.6 and Table 2.

- From this sum, subtract the total ion area counts of the 4-bromofluorobenzene (Surrogate #3) peak.
- Subtract the total ion area counts of all non-APH compounds that are not to be included in the final result.
- Calculate a preliminary mass amount in ng using Equation 20.
- From the preliminary amount (ng), calculate an adjusted mass amount of range hydrocarbons by subtracting the masses of Target APH Analytes which elute in this range (naphthalene), and by subtracting out the mass amount of C_9-C_{10} Aromatic Hydrocarbons.
- Convert the ng value to µg/m³ using Equation 21.

13.3 Additional Calculations

13.3.1 Relative Percent Difference This equation is used for laboratory duplicates and post calibration check of flow controllers when they are received back by the laboratory following sampling.

Equation 22: Relative Percent Difference

$$\frac{x_1 - x_2}{\bar{x}} (100)$$

where:

x_1 First measurement value
x_2 Second measurement value
$\bar{x}$ Average of the two values

13.3.2 Percent Difference This equation is used for the continuing calibration verification standards.

Equation 23: Percent Difference

$$\%D = [(RF_C) - (RF_I)] / [(RF_I)] * 100$$

where:

%D = percent difference
RF_C = response factor from the continuing calibration verification standard
RF_I = average response factor from the initial calibration curve

13.3.3 Percent Recovery This equation is used for the initial calibration verification standard, laboratory control sample, initial demonstration of capability, method detection limit study, and method reporting limit verifications.

Calculate the percent recovery (%R) of the Target APH Analyte or hydrocarbon range using Equation 24.

Equation 24: Percent Recovery

$$\%R = [(C_{found}) / (C_{true})] * 100$$

%R = percent recovery

C_{found} = mass of the analyte or hydrocarbon range detected in the standard (ng)
C_{true} = true mass of the analyte or hydrocarbon range in the standard (ng)

13.3.4 Dilution Factors

Equation 25: Dilution Factor for Pressurization of Subatmospheric Samples:

$$PDF = \frac{P_{atm} + P_f}{P_{atm} + P_i}$$

where:

P_{atm} is the ambient atmospheric pressure, 14.7 psi at sea level.
P_f is the final sample canister pressure, in psig.
P_i is the initial sample canister pressure, in psig. This will most often be a negative value (sub-ambient initial pressure.)

13.3.5 Relative Retention Time

Equation 26: Relative Retention Time (RRT)

$$RRT = \frac{RT_C}{RT_{is}}$$

where:
RT_C Retention time of the target compound, seconds.
RT_{is} Retention time of the internal standard, seconds.

13.4 Data Review The analyst must review data on a real time basis for all calibration and QC data. The QC data must be evaluated by analytical sequence following the data review checklist in Attachment 3. The data shall be reviewed and the sample results calculated and assessed by one analyst and reviewed by a second analyst. The data review checklist is used to document the reviews and once it has been completed, initialed and dated it must be filed with each job file.

Initial calibrations must be reviewed in the same manner as QC data with all ICAL documentation retained in a separate file organized by instrument and date. Refer to the initial calibration checklist in Attachment 2 for the review guideline. The ICAL file must contain all the pertinent information stated in Section 11.1.8.

13.5 Reporting The results of each test shall be reported clearly, unambiguously and objectively, and shall include all the information necessary for the interpretation of the test results and all information required by the reference method and the laboratory quality control program.

In addition to sample results, the APH data report must include the following items:

- Method Blank results
- LCS results
- Sample duplicate results
- Internal standard results (areas) for all field samples and QC samples

13.5.1 Analysis Observations / Case Narrative Summary Form This form, which is included in the *SOP for Sample Analysis, Storage and Tracking*, may be

generated when there are specific sample composition information or analysis issues and/or observations. In addition, during the analysis, specific identification information or problems, interferences, calibration issues, flags, and additional/expanded explanation of flags can be added to the form. This form may be modified as long as the sections and basic concepts are reserved.

Alternatively, information may be included on the Daily QC and Sample Review Checklists (Attachment 3). The form and associated checklists are be used as a means of documentation and will be reviewed when compiling the final report and case narrative. All information regarding the job shall remain in the file, in order that sufficient documentation is available to recreate the job from sample receipt through analysis, data reduction, and reporting.

Any sample flow controller that does not meet the post calibration check criteria (refer to Section 7.2) must be noted so that it may be reported to the client.

13.5.2 Significant Modifications "Significant Modifications" to the APH Method shall include, but are not limited to, any of the following and must be reported accordingly, if they occur.

(1) The use of sample collection devices other than evacuated passivated stainless steel canisters or glass Bottle Vacs (i.e., Tedlar bags).
(2) The use of alternative detectors other than GC/MS to quantify Target APH Analytes and/or hydrocarbon range concentrations.
(3) The use of extracted ions other than 120 and 134 to quantify C9-C10 aromatic hydrocarbons.
(4) The failure to provide all of the data and information required in the report form presented in Appendix 3.

Data produced using an analytical method incorporating any of the "Significant Modifications" described above may *not* be reported as APH data. APH range concentrations are method-defined parameters and as such may only be reported as APH data when produced using the method without "Significant Modifications."

Helium Pressurization – If a canister is pressurized with helium, a correction factor is applied to sample volumes extracted from the canister via auto sampler. This is due to the difference in thermal properties between helium and air. A correction factor worksheet has been generated to determine the exact volume taken from a canister and may be found at J:\\A-GCMS\Helium Pressurization (save the job as P1_____h.xls). Print the sheet and include with the data. Refer to the instruction page in the template for all of the instructions and calculations including backfilled canisters.

13.6 Storing Electronic Data The initial calibration data must be stored in a quantitation method (on the server) using a unique filename and may not be overwritten at any time in order to maintain an accurate audit trail. Therefore, files will be named with a notation indicating the compound list and the date of the corresponding initial calibration. In addition, all data files including method blanks, continuing calibration verification, laboratory control samples and client submitted samples files are saved in a unique sub-directory on the server.

13.7 Sufficient raw data records must be retained of the analysis, instrument calibrations and method detection limit studies including: analysis/calibration date and time, test method, instrument, sample identification, analyte identification, analyst's initials,

concentrations and responses, as well as standards used for the analysis and calibrations, all manual calculations including sample dilutions and manual integrations to permit reconstruction of analyses. Information entered and reported on the quantitation report and instrument run log must be complete and accurate. Retain all daily QC per sequence on file for future reference including tune checks, opening standards, method blanks, laboratory control samples, laboratory duplicates, and initial calibrations and initial calibration verifications. Additionally, all passing QC Canister checks must also be retained on file.

Note: All data records must explicitly connect data to the initial instrument calibration. This includes all samples, continuing calibrations and QC samples.

13.8 The essential information to be associated with analysis, such as computer data files, run logs, etc. shall include: Sample ID code, date of analysis, instrument operating conditions/parameters (or reference to such data), analysis type, all manual calculations including dilutions and manual integrations, analyst's initials, sample preparation (pressure readings and balance gas if pressurized with helium), standard and reagent origin, receipt, preparation, and use, as well as calibration criteria, frequency and acceptance criteria, data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions.

14) Method Performance

14.1 An on-going assessment of method performance is conducted in order to ensure that the laboratory is capable of reporting results which are acceptable for its intended use.

14.2 Method Detection Limit (MDL) This method does not require that MDL studies be performed. However, the APH target compounds are a subset of the EPA TO-15 analysis for which the laboratory performs MDL studies. The procedure used to determine the method detection limits are as stated in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as defined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.* The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the measured concentration is distinguishable from method blank results. The MDL concentrations are listed in Tables 2 of the *SOP for Determination of Volatile Organic Compounds in Air Samples Collected in Specially Prepared Canisters and Gas Collection Bags by Gas Chromatography/Mass Spectrometry (GC/MS).* The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. All MDLs, regardless of the mode of operation, meet the method performance criteria of <0.5ppbV.

14.3 Accuracy and Precision Refer to Section 12.5.1 above for information on replicate precision and accuracy criteria for method performance. Single laboratory accuracy is presented as the second source initial calibration verification standard, which meets the method performance criteria of 30%. Additionally, laboratory generated control limit data for LCSs are presented for the analytes of interest and may be referenced in the TO-15 Method Manual.

14.4 Selectivity Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification.

It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak must be acquired. Scanning also allows identification of unknown compounds in the sample by searching through library spectra.

The sample analysis using the GC/MS is based in part on a combination of retention times and relative abundances of selected ions. The retention time of each chromatographic peak should be ±0.10 minutes of the library/reference retention time of the compound. The acceptance level for relative abundance should be set at ±20% of the expected abundance. The data should be manually examined by the analyst to determine the reason for the # flag [(#) = qualifier out of range], if present and whether the compound should be reported as found or if there is matrix interference. A background subtraction may aid in this determination. Manual inspection of the qualitative results should also be performed to verify concentrations outside the expected range.

Specific selectivity information is provided in this section and document (such as relative retention time) as well as in the referenced method. Refer to the method for additional information on selectivity.

- Use NIST Library 98 or newer version
- The *reference spectra updates* must be performed with every new ICAL utilizing the mid-level standard (minimum). If needed, the reference spectra may be updated sooner with the continuing calibration standard.
- *Retention time updates* must be performed using EasyID and not by updating to the method (InitCal \ Update Calibration). Refer to the Help selection of the software.

14.5 Demonstration of Capability

See Sections 12.5 and 12.6 for initial and ongoing method QC requirements.

15) Pollution Prevention and Waste Management

15.1 Pollution Prevention and Waste Management

All waste disposals shall be carried out in accordance with the requirements detailed in the *SOP for Waste Disposal.* In addition, canisters must be cleaned in accordance with the requirements detailed in the *SOP for Cleaning and Certification of Summa Canister and Other Specially Prepared Containers.*

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 The following is specific information on how to report unacceptable data. If the data requires a data qualifier flag, as specified in this SOP, refer to Appendix D of the most recent version of the Quality Assurance Manual.

Note: No analyte results may be reported with an unacceptable initial calibration or initial calibration verification standard. However, any analyte not meeting such requirements (and the initial calibration is to be used) must be eliminated from the reporting list and any action taken fully documented.

16.2 Continuing Calibration Verification

- When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then

those non-detects may be reported without a qualifier.

- If however, the acceptance criteria for the continuing calibration verification are exceeded low, i.e., low bias, and there are associated samples that are non-detects, then those non-detects may be reported with the reporting limit adjusted to the next level in the calibration curve (typically 5 times higher) to prove the nonexistence of a false negative. If this is the case then a full explanation must be noted in the case narrative of the final report. Refer to Section 13.5 for additional reporting requirements.

16.3 Method Blank

- If an analyte in the blank is found to be out of control and the analyte is also found in associated samples, those sample results shall be "flagged" in the report and the method blank results reported.
- If the analyte is found in the blank but not in the sample then the results for the sample may be reported without a qualifier.

16.4 Laboratory Control Sample All results associated with an out of control laboratory control sample must be reported with the appropriate data qualifier. An indication of whether the LCS was out high or low should also be included.

16.5 Laboratory Duplicate All batch sample results associated with an out of control laboratory duplicate must be flagged with the appropriate data qualifier.

16.6 Internal Standard All target analytes associated with an out of control internal standard must be flagged with the appropriate data qualifier.

16.7 Estimated Sample Results

16.7.1 Sample Hold Time All occurrences of missed holding times must be included on the final report including those samples received and/or analyzed outside of the specified hold times detailed in this standard operating procedure.

16.7.2 Matrix Interference Sample data associated with matrix interference must be flagged with the appropriate data qualifier.

16.7.3 Results Outside Initial Calibration Range All sample results not bracketed by initial calibration standards (within calibration range) must be reported has having less certainty by reporting with the appropriate data qualifier.

17) Training

17.1 All analysts must be trained in accordance with the guidelines detailed in the *SOP for Training Policy.* The training plan (Attachment 1) shall be used to document the training certification of new analysts.

18) Summary of Changes

Table 18.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
11.0	06/02/2018	C. Humphrey	Applied updated SOP formatting style to first two pages and header/footer. Sections renamed and reorganized to align with *SOP for Preparing Standard Operating Procedures*. Section references updated throughout.

			Changed "Summa canister" to "canister" throughout SOP
			5.1 – corrected SOP title
			7.1 – changed "stainless steel pressure vessel" to "passivated stainless steel canister"
			8.8 – expanded list of collection devices
			9.2.1.3 – added holding time requirement for working IS standards prepared in 30L or greater canisters
			11.1 – Table 5 – added Toluene to target APH analytes
			11.9.1 – corrected SOP title
			12.5.2 – revised to align with updated MDL procedure
			12.5.3 – revised to align with updated MDL procedure
			Information previously in section 13 removed – redundant to information covered in section 12
			13.5.1 – revised section to align with current procedure
			13.6 – removed "eight character" notation requirement
			14.2 – revised to align with updated MDL procedure
			15.1 – corrected SOP title
			Information previously in section 17 removed – redundant to information covered in administrative SOPs.
			19.0 – removed references to laboratory SOPs and renumbered
			Attachment 1 – #4 corrected last SOP title
			Attachment 3 – Sample Review Checklist - removed questions 3 and 4 from APH section and renumbered. Revisions made to Sample Review Checklist and Daily QC Review Checklist to match checklists from SOP VOA-TO15

19) References and Related Documents

19.1 *Method for the Determination of Air-Phase Petroleum Hydrocarbons (APH)*, Final Revision 1, Massachusetts Department of Environmental Protection, December 2009.

19.2 2009 and 2016 TNI Standards

20) Attachments

20.1 Attachments

Attachment 1 – Training Plan

Attachment 2 – Initial Calibration Checklist

Attachment 3 – Daily QC and Sample Review Checklists

Attachment 1

Training Plan

Training Plan for Analysis of Air-Phase Petroleum Hydrocarbons (APH) by GC/MS

SOP Title: _____ Revision:_____ Date: _____

Trainee: _____ Trainer: _____ Instrument: _____

1. Read SOP — Trainer ____ Trainee ____ Date _____

2. Read Method — Trainer ____ Trainee ____ Date _____

3. Demonstrated understanding of the scientific basis of the analysis — Trainer ____ Trainee ____ Date _____
   Training Duration _____
   - Whole air sample preconcentration techniques
   - Gas chromatography
   - Mass spectrometry

4. Demonstrated familiarity with related SOPs — Trainer ____ Trainee ____ Date _____
   Training Duration _____
   - SOP for Batches and Sequences
   - SOP for Making Entries onto Analytical Records
   - SOP for Manual Integration Policy
   - SOP for Significant Figures
   - SOP for Nonconformance and Corrective Action
   - SOP for Performing MDL Studies and Establishing Limits of Detection and Quantitation
   - SOP for Cleaning and Certification of Summa Canisters and other Specially Prepared Containers

5. Observe performance of SOP *Training Duration* _____ Trainer ____ Trainee ____ Date _____
   - ___sample preparation/dilution and sample loading and analysis
   - ___analytical sequence setup
   - ___standard preparation
   - ___BFB tuning evaluation/initial calibration/initial calibration verification
   - ___continuing calibration verification
   - ___EnviroQuant introduction
   - ___data reduction and reporting
   - ___canister handling

6. Perform SOP with supervision *Training Duration* _____ Trainer ____ Trainee ____ Date _____
   - ___sample preparation/dilution and sample loading
   - ___analytical sequence setup
   - ___standard preparation
   - ___BFB tuning evaluation/initial calibration/initial calibration verification
   - ___continuing calibration verification
   - ___sample analysis
   - ___EnviroQuant use
   - ___data reduction and reporting
   - ___canister handling

7. Independent performance of the SOP *Training Duration* _____ Trainer ____ Trainee ____ Date _____
   - ___sample loading and sample dilutions
   - ___analytical sequence setup
   - ___standard preparation
   - ___BFB tuning evaluation/initial calibration/initial calibration verification
   - ___continuing calibration verification
   - ___sample analysis
   - ___EnviroQuant proficiency
   - ___data reduction and reporting
   - ___canister handling
   - ___initial demonstration of competency
     - -4 Laboratory Control Samples

8. Instrument operation and maintenance *Training Duration* _____ Trainer ____ Trainee ____ Date _____
   - ___autosample
   - ___GC and capillary column installation
   - ___mass spectrometer
   - ___data system

Attachment 2

Initial Calibration Checklist

Method: **MAPH** Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS_____

ICAL Date: _____ ICAL ID: _____

Air-Phase Petroleum Hydrocarbons
Initial Calibration Review Checklist

Analyst **Reviewer**

☐ 1. Is the required documentation in the ICAL file? ☐
- ☐ BFB Tune analysis Report ☐
- ☐ Calibration Status Report (aka Calibration History) ☐
- ☐ Response Factor Report/Percent RSD (target analytes) ☐
- ☐ Percent RSD Report (hydrocarbon ranges) ☐
- ☐ Quantitation Report for each calibration standard (including manual integration documentation) ☐
- ☐ ICV Quantitation Report ☐

☐ 2. Was the ICAL performed continuously (i.e., not interrupted for maintenance or for sample analysis)? ☐

☐ 3. Have all the calibration standards been analyzed within 24 hours of each other? ☐

☐ 4. Does the BFB tune check standard analysis at the start meet the tune criteria? ☐

☐ 5. Are all the analytes in the blank analysis <MRL? ☐

☐ 6. Does each analyte's ICAL include a minimum of 5 concentrations at 5 consecutive levels? ☐

☐ 7. Were the standards analyzed from low concentration to high concentration? ☐

☐ 8. For each analyte or range, are there no levels skipped? ☐

☐ 9. For each analyte or range, is there only one value used for each calibration level? ☐

☐ 10. For each analyte range, is the lowest std's concentration at or below the analyte's MRL? ☐

☐ 11. If a calibration level is dropped, are all the responses for each target analyte and range dropped and is the information noted in the ICAL explaining the reason? ☐

☐ 12. Is the average RSD ≤30% for all analytes and ranges, except *naphthalene* can be ≤40%? ☐

☐ 13. For the ICV analysis, are all the analytes within 70%-130% recovery? ☐

☐ 14. If there are any manual integrations, are they performed correctly according to the corresponding SOP? If so, initial and date the appropriate pages. ☐

COMMENTS:

Analyst: _____ Secondary Reviewer: _____

Attachment 3

Daily QC and Sample Review Checklists

EPA Compendium Method TO-15 - Daily QC Review Checklist

(Note exceptions in Comments and include Analysis Observations/Case Narrative Summary Form as appropriate)

Method: ☐ EPA TO-15 ☐ EPA TO-14A **Analysis Date:** _____

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan **Scan Low Level (0.1ng):** ☐ Yes ☐ No **DOD:** ☐ Yes ☐ No

Analyst **Reviewer**

☐ 1. Is the required documentation present? ☐
- ☐ CORRECT BFB Tune analysis Report
- ☐ CCV analysis Quantitation Report & %D Report
- ☐ LCS analysis Quantitation Report
- ☐ MB analysis Quantitation Report

☐ 2. BFB **tune** check standard analysis meet the tune criteria for the method indicated above? ☐

☐ 3. Analyses within the tune's **24-hr window or** ☐ **Client's 12hr window requirement**? ☐

☐ 4. Does the **CCV** have a difference ≤30% for all analytes? ☐
[Note all outliers biased high and/or low]

☐ 5. **DoD**: Does the **Closing CCV** have a difference ≤30% for all analytes? ☐
[Note all outliers biased high and/or low]

☐ 6. All **IS** retention times within 20 seconds of the CCV RT or the RT from the midpoint (ICAL)? ☐

☐ 7. All **IS** responses within ±40% of CCV or the midpoint in the ICAL? ☐

☐ 8. All **surrogate** recoveries (in CCVs, MB, LCSs, etc.) within acceptance limits (70%-130%) ☐

☐ 9. All analytes in the **MB** <MRL? (DoD <1/2MRL, except Acetone, MeCl2, EtOH, Carbon Disulfide)? ☐

☐ 10. **LCS** %R within the lab control limits for all analytes except AZ samples (70%-130%, VA 50%-150%)? ☐

☐ 11. All analytes in the **Lab Duplicate / DLCS** within ±25% or the client specified limits? ☐

☐ 12. **DoD/Navy**: **DLCS** analyzed? ☐

Air-Phase Petroleum Hydrocarbons

☐ 1. Does the **CCV** meet the following criteria? ☐
- Percent difference ≤30%.
- One compound or range can be >30%, but less than 50%.
- No single analyte or range may be >50%.

[Note outliers biased high and/or low in comments below]

☐ 2. Does lab **duplicate** meet an RPD of ≤30% for results >5x MRL? Repeat analysis if: ☐

RPD >30 (where both analyses are >5x RL	1st analysis detect @ >5x MRL, Dup=ND
1st analysis ≤5x RL; Dup=ND (RPD not calculable)	

☐ 3. Are the analytes in the **LCS** within 70%-130% recovery? ☐

COMMENTS:

Analyst/LIMS Run Approval: _____ Secondary/LIMS Supervisor Approval: _____

EPA Compendium Method TO-15 – Sample Review Checklist

(Note exceptions in Comments and include Analysis Observations/Case Narrative Summary Form as appropriate)

Method: ☐ EPA TO-15 ☐ EPA TO-14A **Analysis Date:** _____ **Project #:** _____

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan **Scan Low Level (0.1ng):** ☐ Yes ☐ No **DOD:** ☐ Yes ☐ No

Analyst		**Reviewer**
☐	1. All analyte hits in the samples within the **calibration range** and/or noted?	☐
☐	2. All **peak integrations** acceptable?	☐
☐	3. All **manual integrations** flagged and documented?	☐
☐	4. Have **Q values** been verified for each peak?	☐
☐	5. All **calculations** correct?	☐
☐	6. Has the analyst initialed and dated each **quantitation report**?	☐
☐	7. For **TICs** are the relative intensity and other requirements met (associated MB reported)?	☐
☐	8. **Auto report** correct?	☐
☐	9. **MRL** = _____ ☐ ng ☐ pg (ethanol, acetone, vinyl acetate = 5.0ng)	☐
☐	10. Pressurized with **Helium**? Is the worksheet completed for all samples?	☐
☐	11. Report to **MDL**? ☐ Yes ☐ No	☐
☐	12. **Global Minimum Detection Limit** = _____ ☐ ng ☐ pg	☐
☐	13. **DOD:** Are **manual integrations** notated in the **case narrative?**	☐

Air-Phase Petroleum Hydrocarbon

☐	1. Are all manual **integrations** flagged and documented (except for HC ranges)?	☐
☐	2. Are the associated ICAL responses correct?	☐
☐	3. Does the lab **duplicate** meet a RPD of ≤30% for results >5x the MRL? Otherwise, repeat analyses if:	☐

RPD >30 (where both analyses are >5x RL	1st analysis detect @ >5x MRL, Dup=ND
1st analysis ≤5x RL; Dup=ND (RPD not calculable)	

COMMENTS:

☐ 1. **CASE NARRATIVE COMPLETED?** ☐

Analyst/LIMS Run Approval: _____ Secondary/LIMS Supervisor Approval: _____

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN AIR SAMPLES COLLECTED IN SPECIALLY PREPARED CANISTERS AND GAS COLLECTION BAGS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

DOCUMENT I.D. VOA-TO15

Approved By: Kate Kaneko Date: 8/6/18
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Doc Control ID:	Uncontrolled	Archived Date:	

TABLE OF CONTENTS

1) Scope and Applicability

1.1 This procedure is based on and incorporates the requirements detailed in EPA Compendium Methods TO-15 and TO-14A and is used to quantify a wide range of volatile organic compounds (VOCs) in gaseous matrices collected in gas collection bags (method modification) and specially prepared stainless steel canisters or glass bottles. This method typically applies to ambient concentrations of VOCs 0.50ug/m3 (down to 0.10ug/m3 for low level ambient analyses) and above for the SCAN mode and 0.010ug/m3 and above for the SIM mode; however, refer to Tables 3 and 3A for the specific laboratory initial calibration ranges for each target compound. The method requires VOC enrichment by concentrating up to one liter of a sample volume, with a virtually unlimited upper concentration range using dilutions from source level samples.

In this document, Tables 2 and 2A (see Note 1 below) list compounds that can be determined by this procedure along with their corresponding laboratory method reporting limits (MRLs) and method detection limits (MDLs). The reported MRL may be adjusted higher; however, the capability of achieving lower MRLs for specific project requirements must be thoroughly demonstrated (by an acceptable initial calibration and method reporting limit check standard) and documented as long as the MRL is higher than the current method detection limit for each compound. Additional compounds may be analyzed according to this procedure as described in the referenced methods as long as the requirements of this document are adhered to. The number of samples that may be analyzed in a 24-hour period is about twenty. The number of sample results that may be reduced in an eight-hour day is approximately twenty.

2) Summary of Procedure

2.1 The analytical method involves using a high-resolution gas chromatograph (GC) coupled to a mass spectrometer (MS). The GC/MS utilizes a linear quadrupole system, which allows for it to be operated by either continuously scanning a wide range of mass to charge ratios (SCAN mode) or by Select Ion Monitoring mode (SIM), which consists of monitoring a small number of ions from a specified compound list.

An aliquot of an air sample is concentrated on a solid adsorbent trap (either cryogenically or fan cooled glass beads or stronger adsorbents at higher temperatures) to collect the analytes of interest. To remove co-collected water vapor, the concentrated sample then goes through a water removal (dry purge) step. After the sample is pre-concentrated on a trap, the trap is heated and the VOCs are thermally desorbed onto a refocusing cold trap. The VOCs are then thermally desorbed onto the head of a capillary column once the cold trap is heated. The oven temperature (programmed) increases and the VOCs elute and are detected by the mass spectrometer.

Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This method utilizes the internal standard calibration technique; refer to Section 3.16 for a complete definition.

3) Definitions

3.1 Cryogen A refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Liquid nitrogen (cryogen) is used for this purpose and it has a boiling point of -195.8°C.

3.2 Gauge Pressure Pressure measure with reference to the surrounding atmospheric (barometric) pressure, usually expressed in units of psig. Zero gauge pressure is equal to atmospheric pressure.

3.3 MS-SCAN Mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

3.4 MS-SIM Mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

3.5 Analytical Sequence The analytical sequence describes exactly how the field and QC samples in an analytical batch are to be analyzed.

3.6 Neat Stock Standard A purchased, single component assayed reference material having a stated purity used to prepare working calibration standards.

3.7 Stock Standards Solution A concentrated solution of one or more target analytes at a known concentration purchased from a reputable commercial vendor. Stock standard solutions are used to prepare working calibration standards.

3.8 Intermediate Calibration Standard A solution of one or more target analytes at a known concentration prepared either from one or more neat stock standards or from one or more stock standards solutions.

3.9 Working Calibration Standard A solution of all the target analytes at a known concentration prepared either from one or more intermediate calibration standards and/or from one or more stock standard solutions.

3.10 Calibration or Standard Curve A calibration or standard curve is a graph which plots the concentration of a compound (or an analyte) versus the instrument response to the compound.

3.11 Initial Calibration Verification (ICV) Standard A solution prepared in the laboratory containing known concentration(s) of analytes of interest. The solution is prepared from neat stock standards and/or stock standards solutions which are from a different source than the standards used to prepare the working calibration standards.

3.12 Continuing Calibration Verification (CCV) Standard A working calibration standard which is analyzed at specific intervals in order to verify that the instrument continues to meet the calibration criteria.

3.13 Field Sample A sample collected and delivered to the laboratory for analysis.

3.14 Manual Integration This term applies to a data file in which setpoints have been changed and reintegration has occurred under the changed setpoints; baselines have been adjusted; peak integration start and stop "ticks" have been changed; peak area, or peak height, are changed after the time of data collection and data file generation.

3.15 Batch Quality Control (QC) Batch QC refers to the QC samples that are analyzed in an analytical batch of field samples and includes the Method Blank (MB), Laboratory Control Sample (LCS) and Laboratory Duplicate (LD).

3.16 Internal Standard Calibration Compares the instrument responses from the target compound in the sample to the responses of specific standards (called internal standards), which are added to the sample or sample preparation prior to analysis. The ratio of the peak area (or height) of the target compound in the sample or sample preparation is compared to a similar ratio derived for each calibration standard.

3.17 May This action, activity, or procedural step is neither required nor prohibited.

3.18 Must This action, activity, or procedural step is required.

3.19 Shall This action, activity, or procedural step is required.

3.20 Should This action, activity, or procedural step is suggested, but not required.

3.21 SOP Standard Operating Procedure

3.22 Service Request A form generated, at the time of sample receipt, which details pertinent information such as client name, address, contact, client and laboratory sample identifications, sampling and receipt dates and times, requested analyses, sample type, canister pressures (initial and final), and the service request number (unique number for each submitted job) and serves as an inter-laboratory "custody" form which accompanies all samples throughout the laboratory.

3.23 Selectivity Selectivity of a method refers to the extent to which it can determine particular analyte(s) in a complex mixture without interference from other components in a mixture. Another definition is the extent to which a particular method can be used to determine analytes under given conditions in the presence of other components of similar behavior.

3.24 Limit of Detection (LOD) The smallest amount or concentration of a substance that must be present in a sample in order to be detected at a high level of confidence (99%). At the LOD, the false negative rate (Type II error) is 1%. (DoD Clarification). For consistency purposes, the LOD may be referred to as the MDL once it is reported; however, full verification will be on file in the laboratory per the procedures detailed in this document.

3.25 Limit of Quantitation (LOQ) The lowest concentration that produces a quantitative result within specified limits of precision and bias. For DoD projects, the LOQ shall be set at or above the concentration of the lowest initial calibration standard. (DoD Clarification). For consistency purposes and since the LOQ and MRL are equivalent with regards to laboratory procedure, the LOQ will be referred to as the MRL in this document and once it is reported. Full verification will be on file in the laboratory per the procedures detailed in the document.

3.26 Detection Limit (DL) / Method Detection Limit (MDL) The smallest analyte concentration that can be demonstrated to be different from zero or a blank concentration at the 99% level of confidence. At the DL, the false positive rate (Type 1 error) is 1%. (DoD Clarification). For consistency purposes, the DL may be referred to as MDL. Also, as far as reporting is concerned the MDL will be raised up (where necessary) to the verified LOD per the procedures defined in this document and reported accordingly.

4) Responsibilities

4.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP may perform analysis, interpretation and peer review of the results. Data reduction and/or peer review may be performed by another qualified employee. This employee must be

familiar with the analytical technique and have completed a data review training plan to ensure familiarity with specific analysis and requirements.

4.2 The supervisor/manager must ensure that method proficiency is documented initially and whenever significant changes in the instrument type, personnel, and matrix or test method are made.

4.3 The department supervisor/manager or designee shall perform final review and sign-off of the data.

5) Interferences

5.1 Canisters

Canisters shall be stored in a contaminant free location and shall be capped tightly during shipment to prevent leakage and minimize any compromise of the sample. The pressure/vacuum is checked prior to shipment and upon receipt from the field. Any problems with the sample from the field are noted and the Project Manager contacted.

Also, canisters must be cleaned and certified to be free from target analytes before being shipped to the field for sample collection. The procedure is described in detail in the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters* (refer to this procedure as well as Section 12.7 for the acceptance criteria).

Current laboratory practice entails the segregation of 6L canisters into ambient (low) level and source levels. All the ambient canisters are used for low level (indoor air, ambient air) projects and not intentionally for soil gas, SVE monitoring, or other higher level applications. It may be necessary to "retire" an ambient canister and re-assign for source level use if high concentrations are encountered. This decision will be made by management based on analytical concentrations and what compounds were encountered at these levels. If the level of any analyte is detected above 5,000ug/m*3* in the ambient can, then the supervisor/team leader must be contacted to determine if the canister(s) is to be retired. If retirement is decided upon, make a notation on the sample tag (or other color coded tag) of each canister in question. The notation must contain the analyte, threshold levels and retirement from ambient use (initial and date notation) so that the canister conditioning/management department may properly execute the retirement.

5.2 Analytical System

The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with buna-N rubber components must be avoided.

5.3 Carbon Dioxide

Excessive levels of carbon dioxide present in a sample may interfere with analysis by freezing up the cryogenic trap. A smaller aliquot must be analyzed to eliminate this problem, or the sample should be analyzed using the higher temperature multi-adsorbent trapping technique which allows carbon dioxide to pass.

5.4 Gas Collection Bags

This procedure covers the use of gas collection vessels such as Tedlar® or Mylar® bags. However, due to the nature of these types of bags it is not recommended that clients use this option for ambient air samples. Sample collection bags made out of Tedlar®

have contaminants that are inherent to the manufacturing process. The two main contaminants are phenol and N,N-Dimethylacetamide. However, this only becomes a problem when the concentration levels in the sample are low ppbv such as ambient air monitoring samples where more of the sample usually has to be concentrated and analyzed. To minimize the loss of sample integrity, a 72-hour hold time has been incorporated into the procedure.

5.5 Glassware

Interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware results in discrete artifacts and/or elevated baselines in the detector profiles should be minimized. All glassware associated with this method must be scrupulously cleaned to avoid possible contamination. The cleaning shall be performed in accordance with the procedure outlined in the *SOP for Glassware Cleaning.* The use of high purity water, reagents, and solvents helps to minimize these problems.

6) Safety

6.1 Each compound, mixture of compounds, standards, and surrogates, as well as samples, should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest level possible through the use of gloves (to minimize absorption through the skin) and hoods (to minimize inhalation). Refer to the laboratory waste management plan for the safe disposal of chemicals and samples.

6.2 Safety Data Sheets (SDS)

The analyst should consult SDS for compounds being handled in the course of this procedure, and be familiar with proper safety precautions to be followed when handling hazardous chemicals. Care should be taken when handling standard material in a neat or highly concentrated form.

6.3 Liquid Nitrogen

Liquid nitrogen can cause serious tissue damage (frostbite) with only a few seconds of contact. The valves on the cryogen dewars should be opened slowly so leaky fittings can be identified. Neoprene or leather gloves should be worn when turning valves and handling tubing and fittings that have been in contact with the cryogen.

6.4 Protective Clothing

Personal protective clothing (safety glasses, gloves and lab coat) are required when preparing standards and handling standard material in neat form.

6.5 Pressurized Gases

The use of pressurized gases is required for this procedure. Care should be taken when moving cylinders. All gas cylinders must be secured to a wall or an immovable counter with a chain or a cylinder clamp when not in use. The regulator should never remain on small “D” size cylinders following use. Sources of flammable gases (i.e. pressurized hydrogen) should be clearly labeled.

6.6 Syringes

The proper use of syringes should be part of employee training for this SOP. Care should be taken to avoid personal injury as a result or improper handling techniques.

7) Sample Collection, Containers, Preservation, and Storage

7.1 Air samples are collected in the field and delivered to the laboratory and shall be collected in either a specially prepared, leak-free, passivated stainless steel canister (with valve) of desired volume (e.g., 6L), a glass sampling bottle (Bottle Vac, Entech Inntruments) or a sample collection bag (Tedlar). Canister samples may either be grab or time integrated (using a variable flow controller, refer to the *SOP for Flow Controllers and Critical Orifices*) utilizing the canister vacuum to draw the sample. Bags require the use of an upstream pump or a "lung machine."

7.2 There are no special preservation requirements for either canisters, Bottle Vacs or bags. However, bags should be stored in an environment free from puncture or deterioration sources (by hanging them from clips), labeled with the specific service request number, in accordance with the *SOP for Laboratory Storage, Analysis and Tracking*. Canisters and bottles should be stored on the appropriate shelves until they are to be analyzed.

7.3 Sample collection bags must be analyzed within 72 hours from the confirmed time of sampling. Samples received by the laboratory shall be analyzed within 30 days of sampling or sooner if project specific requirements dictate. Programs, which have shorter recommended or required hold times, include the Department of Toxic Substances Control (DTSC), which advises a 72 hour hold time. The Minnesota Pollutions Control Agency (MPCA) and EPA Region 9 both require a 14 days hold time. Additionally, the MPCA does not allow the use of Tedlar bags for sampling or sample dilution. The DTSC requirement is an advisory notice, but the laboratory shall make every effort to comply. However, the following statement shall be added to each report where sample analyses do not meet the 72 hour hold time and the client project is intended to comply with DTSC requirements. "The recommended 72-hour hold time for the analysis of TO-15 was exceeded per the DTSC and LARWQCB Advisory – Active Soil Gas Investigations document dated January 28, 2003; however, this specific hold time statement is advisory and not considered as regulation. In addition, the samples were analyzed within the EPA Method TO-15 stated requirement of 30 days."

8) Apparatus and Equipment

8.1 Additional instruments and/or differing models may be utilized as long as they are equivalent and meet the minimum requirements of this document.

8.2 Gas Chromatograph (GC)

An instrument capable of temperature programming, with a column oven that may be cooled to sub-ambient temperature at the start of the gas chromatographic run to result in the resolution of the VOCs.

Hewlett Packard 5890 Series II Plus
Hewlett Packard 6890 Series
Hewlett Packard 6890A Series
Agilent 6890N Series
Agilent 7890A Series
Agilent 7890B Series

8.3 Autosampler

Tekmar-Dohrmann AUTOCan Autosampler: 14-ACAN-074

Markes Autosampler:	UNITY 2/CIA Advantage
Concentrating Trap (cryogenic trap, built-in):	14-6938-020
Cryofocusing Module w/split valve:	14-6520-A00
GAST Vacuum Pump:	DOA-P104-AA or equivalent

8.4 Mass Spectrometer (MS)

A MS capable of scanning from 34 to 350 amu every second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Bromofluorobenzene (BFB) which meets all of the criteria when 50ng or less of BFB is injected onto the GC/MS system.

Hewlett Packard 5972 Series
Hewlett Packard 5973 Series
Agilent 5973N
Agilent 5973 *inert*
Agilent 5975B *inert*
Agilent 5975C *inert*
Agilent 5977A

8.4.1 Ionization Gauge Controller

- Agilent: 59864B
- Granville-Phillips 330 Ionization Gauge Controller: 330001/2/3
- Hewlett Packard Ionization Gauge Controller: 59864B

8.5 Analytical Column

Any analytical column capable of separating the compounds of interest may be used. The capillary column should be directly coupled to the source of the mass spectrometer. The following are suggested columns; an alternative column may be used as long as sufficient peak resolution and separation is achieved.

- Restek Rxi-1ms Fused Silica Capillary Column; 30m x 0.25mm ID 1.0µm film thickness

  OR

- Restek Rxi-1ms Fused Silica Capillary Column; 60m x 0.25mm ID 1.0µm film thickness

8.6 Data Systems

IBM-compatible PC with Windows 95/98/NT/XP/7 (Microsoft Office EXCEL version 2003 or newer) and Hewlett Packard Chemstation software including EnviroQuant with Extracted Ion Current Profile (EICP), National Institute of Standards and Technology (NIST) library (2011 version or newer) or equivalent.

8.7 Canister Pressurization Station

Vacuum/Pressure Gauge [0 to –30 inHg; 0-90 or 100 psig]

8.8 Canister Sampling Devices

Refer to the *SOP for Flow Controllers and Critical Orifices* for specific calibration and other pertinent information.

- VICI Condyne Model 300 Flow Controller
- Critical Orifices (Laboratory manufactured)

8.9 Gas Collection Devices

- Lab Commerce, Aerosphere Model S6L, 6.0L Passivated Canisters or equivalent
- Lab Commerce, Stabilizer Model 22.4L, 2.4L Canisters or equivalent
- Restek Corporation, #24203, 3.0L Silco Canisters or equivalent
- Tedlar bags – 0.5L, 1L, 3L, 5L, 10L, 25L, and 40L (other sizes are available; however, the volumes that are listed encompass the majority of the bags supplied and the samples submitted to the laboratory).
- Entech Instrument, SiloniteTM Canisters or equivalent
- Entech Instruments, Bottle Vacs or equivalent

8.10 Dynamic Dilution System

- Entech Dynamic Diluter Model 4620A
- Toshiba laptop computer Model 2210CDT/6.0 and Software NT460

9) Standards, Reagents, and Consumable Materials

9.1 Reagents and Equipment

9.1.1 UHP Grade Helium (99.999%) (GC carrier gas, preconcentrator purge/sweep gas, pressurization gas)

9.1.2 Cryogen - Liquid nitrogen from bulk tank or 50 psig dewars (used to cool preconcentrator traps)

9.1.3 UHP/Zero Grade Air (canister pressurization)

9.1.4 ASTM Type II Water, DI water or equivalent

9.1.5 UHP Grade Nitrogen (99.999%) (additional pressurization gas, based on other methods requested – modification to method)

9.2 Standards

Standards are prepared for both SCAN and Selective Ion Monitoring (SIM) modes according to the procedures detailed in this section. The preparation of standards for the analysis of air samples is carried out by following the procedure, "Preparation of Gas Phase Standards for Ambient Air Analysis", Application Note, Spring 96, Vol. 6.5, *Tekmar*-DOHRMANN AutoCan User's Manual. Neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

9.2.1 Instrument Performance Check, Internal Standard and Surrogate Spiking Mixture
Prepare a standard solution of p-Bromofluorobenzene (BFB-used as both a tune check and surrogate compound), bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene, 1,2-dichloroethane-d4(surrogate), and toluene-d8(surrogate) at 500μg/m^3 each in humidified zero air (Section 8.2.1.2). Prepare this standard according to the procedure outlined in Volume 6.5 of the *Tekmar*-

DOHRMANN Application Note. This standard may also be prepared from a neat cocktail as in Section 9.2.2.2.1 or as stated in Section 9.2.1.3.

9.2.1.1 An intermediate standard is prepared from neat compounds in a glass static dilution bottle (SDB). After the volume of the SDB is determined, calculate the mass of each compound to be spiked to achieve a final concentration of 5.0µg/ml. Then use the density of each neat compound to calculate the microliter amount to be spiked into the SDB. The SDB is then heated for a minimum of one hour at ~60˚C to completely volatilize all components.

Concentration of the intermediate standard prepared in a SDB is 5.0µg/mL. The amount required to achieve this concentration is determined through the use of the following equation.

$$A = \frac{(C)(V)}{D} \qquad \text{(Equation 1)}$$

Where:

A Amount of each compound required to achieve the desired concentration of the standard in the SDB (µL)
C Desired concentration of SDB (µg/mL)
V Actual volume of the SDB (mL)
D Density of the compound in question (µg/µL)

Example:

Calculate the amount of neat bromochloromethane needed to achieve the final concentration of 5.0µg/mL of that compound in the SDB.

V = 2010mL
D = 1934.4µg/µL
C = 5.0µg/mL

$$A = \frac{\left(5.0\,\frac{\mu g}{mL}\right)2010\,mL}{1934.4\,\frac{\mu g}{\mu L}} = 5.2\mu L$$

Density (µg/µL)	Compound
1934.4	Bromochloromethane
1170.1	1,4-Difluorobenzene
1157	Chlorobenzene-d5
1307	1,2-Dichloroethane-d4
943	Toluene-d8
1593	BFB

9.2.1.2 The Working standard is prepared in a canister by spiking an aliquot of the stock SDB standard (Section 9.2.1.1) using a heated gastight syringe. Connect a cleaned, evacuated canister to a source of pure diluent gas (humidified zero air) using a Teflon line with a stainless steel tee directly above the canister valve. One port of the tee is fitted with a septum. Spike the SDB stock and following removal of syringe a small flow of diluent gas to flush the spike into the can. Pressurize the can to positive 83.3 psig with humid zero air, and allow the contents to equilibrate for approximately 24 hours before using.

Concentration of the working standard prepared in a canister is 500ng/L. The final pressure of the canister is 83.3psig; therefore, the pressurized volume is 40L, which is obtained through the use of the following equation.

PV = PDF(V) (Equation 2)

Where:

PV Pressurized canister volume (L)

PDF Pressure Dilution Factor, where PF = $\frac{P_{atm} + P_f}{P_{atm} + P_i}$

P_f Final Canister Pressure

P_i Initial Canister Pressure

V Volume of canister at 1atm

P_{atm} Atmospheric Pressure = 14.7psig

Example:

$\frac{14.7 + 83.3}{14.7 + 0}(6L)$ = 40L

In order to prepare the canister with a concentration of 500ng/L, it must be determined how much of the intermediate standard is required. This is achieved through the use of the following equation.

$$A = \frac{(F)(V)}{(C)\left(1000\frac{ng}{\mu g}\right)}$$ (Equation 3)

Where:

F Desired concentration of working standard (ng/L)

V Pressurized Volume of Canister (L)

C Concentration of prepared SDB (µg/mL)

A Amount of standard (mL) of the SDB required to obtain the desired working standard concentration

Example:

$$A = \frac{500\frac{ng}{L}(40L)}{\left(5.0\frac{\mu g}{mL}\right)\left(1000\frac{ng}{\mu g}\right)} = 4mL$$

9.2.1.3 Currently the working standard is purchased in a cylinder at a certified concentration of 500ng/L (prepared by Linde SPECTRA Environmental Gases, Alpha, NJ).

The internal standard (IS) cylinder comes from the vendor with a one year expiration date. These compounds should be stable in the high-pressure cylinder for five years or longer so the laboratory will extend the expiration date to two years from the date of preparation. The working standards are canisters filled directly from the main cylinder and are given a two month expiration when prepared in a 6L canister and a six month expiration when prepared in a 30L or greater canister. The method utilized relative response factors for target analyte quantitation so the IS concentrations are factored out since they appear in the numerator and denominator of the final calculation.

A quantitation report with chromatogram of a TO-15 blank run will be printed as soon as a new IS cylinder is put into use and again after one year. The latter will be checked for any unexpected peaks to look for possible degradation of the IS compounds in the cylinder. These shall be kept on file with the original certificate of analysis.

9.2.1.3.1 For SCAN analyses, the working standard is filled directly into a canister to a pressure of 70 to 80 psig.

9.2.1.3.2 For SIM analyses, the working standard is diluted and pressurized with humid zero air to the desired concentration using Equation 2 in Section 9.2.1.2. Typical concentrations will be 20ng/L, 40ng/L or 50ng/L.

9.2.2 Initial Calibration (ICAL) Standard Prepare the primary source calibration standards in canisters with nominal concentrations of 1ng/L (optional), 20ng/L and 200ng/L for analyses in SCAN mode and 0.1ng/L, 5.0ng/L, and 200ng/L for analyses in Selective Ion Monitoring (SIM) mode for each of the target analytes. Differing injection volumes will create the standard concentrations listed in Tables 3 (SCAN) and 3A (SIM) of this document. The full list of analytes which are analyzed according to this method can also be found in Tables 2 (SCAN) and 2A (SIM).

Standards are prepared by diluting the stock standard with humid zero air into a canister. The stock standard is a certified custom-blended cylinder (prepared by Linde SPECTRA Environmental Gases, Alpha, NJ). Refer to Tables 3 and 3A for the list of analytes and certified concentrations in the purchased cylinder.

9.2.2.1 Working standards are prepared into canisters using the Entech Dynamic Diluter. Turn on the power to the diluter one hour prior to using to allow for the components to come to thermal equilibrium. Connect the

computer and start the software. Connect a Zero Air source to the humidification chamber (flow controller #1). Connect stock standard cylinder#1 to flow controller #2 inlet. Open the cylinder valves. Adjust the inlet pressures to 50 to 60psig.

Standard Concentration Selection: The concentration of the three working standards prepared in canisters should be 200ng/L, 20ng/L and 1ng/L (depending on the dynamic range of the initial calibration include 1ng/L if a 0.08ng and 0.4ng on column standard is desired or this standard may be used for the 0.5ng/L concentration as well) for SCAN and 0.2ng/L, 4.0ng/L, and 200ng/L for SIM.

Position 1 – Total Air Flow (Zero Air)
Position 2 – Standard Flow (Purchased Standard One)
Position 3 – Standard Flow (Purchased Standard Two if Applicable)
Position 4 – Total Air Flow (Zero Air) (utilized if preparing a two dilution standard)
Position 5 – Diluted Standard Flow (utilized if preparing a two dilution standard)

Step1: Determine the required flow rate of the stock standards (positions #2 and #3). The range must be from 5 to 50sccm (standard cubic centimeters per minute, same as ml/min). The flows listed below are guidelines to be used for the default standard flow (based on the desired standard concentration) and were chosen based on the ultimate final dilution required and limitations of the Dynamic Diluter (flows must be from 150 to 2000ml/min.).

Desired Standard Conc.	Default Standard Flow
200ng/L	50ml/min
100ng/L	50ml/min
20ng/L	20ml/min
5.0ng/L	10ml/min
4.0ng/L	8ml/min
1ng/L	50ml/min; 20ml/min (See Note 1 below)
0.2ng/L	10ml/min; 20ml/min (See Note 1 below)

Note 1: For the 1ng/L and 0.2ng/L standards (or any standard requiring more than a 400X dilution of the stock), a slightly different procedure is performed. In order to prepare these standards, a double dilution must be performed which involves taking the primary dilution flow and making a secondary dilution of that using the diluent gas. Unscrew the cover of the dilutor and connect the first mass flow controller as well as the tubing to re-route the first dilution output from the final standard canister to the 2nd dilution chamber. Refer to example 2 for the calculation guidelines to prepare a two dilution standard.

Example 1: Prepare a 200ng/L working standard. The concentration of each stock standard is 1000ng/L.

Step 2: Determine the required dilution factor for each stock.
Dilution factor = Stock Conc. (ng/L) / Desired Standard Conc. (ng/L)
Dilution Factor = 1000ng/L / 200ng/L = 5

Step 3: Calculate Total Flow
Total Flow= (stock std. flow-see table above)*(Dilution Factor)
Total Flow=50ml/min*5 = 250ml/min

Step 4: Calculate Diluent Air Flow
Air Flow=Total Flow-(Sum of stock std. flows-purchased cylinders)
Air Flow=250ml/min-(50+50)ml/min = 150ml/min

Example 2: Prepare a 0.2ng/L working standard. The concentration of each stock standard is 1000ng/L.

Step 2: Determine the required total dilution factor for the 0.2ng/L standard.
Dilution factor = Stock Conc. (ng/L) / Desired Standard Conc. (ng/L)
Dilution Factor = 1000ng/L / 0.2ng/L = 5,000

The two dilutions must be performed which total the dilution factor calculated above. Since the flow for the Diluter is restricted to a maximum of 2000ml/min, the total flow (as calculated in Step 3 below) cannot exceed 2000ml/min; therefore, the dilutions must be chosen accordingly.

Step 3: Calculate Total Flow
Total Flow = (stock std. flow-see table above)*(Dilution Factor)
Total Flow (Dilution 1) = 10ml/min*200 = 2000ml/min

For the 2nd dilution take the stock standard flow selected for dilution 1 for the two purchased cylinders (10ml/min each based on the desired final concentration) and add them together (10ml/min + 10ml/min for 20ml/min) to get the stock standard flow for the 2nd dilution.

2nd Dilution Factor Needed = Total Dilution/1st Dilution
2nd Dilution Factor = 10000/200(1st dilution) = 50
Total Flow (Dilution 2) = 20ml/min*50 = 1000ml/min

Step 4: Calculate Diluent Air Flow
Air Flow=Total Flow-(Sum of stock std. flows-purchased cylinders)
Air Flow=2000ml/min-(10+10)ml/min = 1980ml/min (Dilution 1)
Air Flow=1000ml/min-20ml/min = 980ml/min (Dilution 2)

Position 1 = 1980ml/min
Position 2 = 10ml/min
Position 3 = 10ml/min
Position 4 = 980ml/min
Position 5 = 20ml/min

Step 5: Enter flow rates in the appropriate fields in the Entech software. Start flows by clicking the "GO" button in the top right of the window. Allow flows to equilibrate for at least fifteen minutes, then attach an empty canister to the outlet port and open the valve. The outlet pressure will be displayed in the lower right of the window, in units of psia. Close the canister valve when the pressure reaches 30psia. There is a relief

valve on the diluter that will open when the pressure reaches 35psia, so the canister will still be usable if the valve is not closed in time.

9.2.2.2 When analysis of additional (extra) compounds are requested which are not in the purchased stock cylinders, the following preparation instructions should be used. In addition, the internal standard / surrogate standard may also be prepared in this manner (Sections 9.2.2.2.1 – 9.2.2.2.2) as mentioned in Section 9.2.1.

9.2.2.2.1 *Equi-mass "soup"* (contains compounds in equal mass amounts) or *cocktail* prepared from the neat compounds for a large number of components. If additional SIM compounds are requested, the same cocktail may be used.

Cocktail Preparation:

Step 1: This cocktail is prepared by combining 25mg of each neat compound into a small glass vial. Use a microliter syringe to transfer each compound, cleaning with solvents in between. Put the vial in the freezer between aliquots to minimize volatilization. Take the density of each compound into account to determine the actual amount of each compound to spike into the cocktail by using the following equation.

$$S = \frac{A}{D} \qquad \text{(Equation 4)}$$

Where:

S Actual spike amount (µL)
A Desired amount for each compound (mg)
D Density (mg/µL); refer to Table 2 for the density

Example: The actual volume of acrolein to add to the cocktail is calculated by the following.

$$S(\text{Acrolein}) = \frac{25mg}{\left(0.840\ \frac{mg}{\mu l}\right)} = 29.8\mu L$$

Step 2: The concentration of each compound in the cocktail is determined by the following equation.

$$C = \frac{A}{V}\left(1000\ \frac{\mu g}{mg}\right) \qquad \text{(Equation 5)}$$

Where:

C Concentration of cocktail (µg/µL)
A Amount of each compound (mg)

V Final volume of cocktail (total spike volumes of each compound) (µL)

Example:

$$C = \frac{25mg}{631.8\mu L}\left(1000\frac{\mu g}{mg}\right) = 39.569\mu g/\mu L$$

9.2.2.2.2 *An intermediate standard* is prepared from neat compounds by spiking individual compounds into a glass static dilution bottle (SDB) as described in Section 9.2.1.1 or spiking an aliquot of a cocktail into the SDB. The spike amount of a cocktail is determined by using the following equation.

$$S = \frac{C_1 V}{C_2} \qquad \text{(Equation 6)}$$

Where:

S Spike amount required in order to obtain the desired concentration (µL)
C_1 Desired concentration of SDB (µg/mL)
C_2 Concentration of cocktail (µg/µL)
V Volume of SDB (L)

Example: Determine the spike amount of the cocktail required to achieve the desired intermediate standard concentration.

$$S = \frac{\left(1\frac{\mu g}{ml}\right)(2010ml)}{27.81\frac{\mu g}{\mu L}} = 72.28\mu L$$

9.2.2.2.3 *Intermediate Standard Preparation (Gaseous Compounds*) As an alternative to the glass SDB method, if the extra compounds needed to be analyzed are gases at room temperature, use a gastight syringe to prepare an intermediate standard in a 1L Tedlar bag filled with humidified zero-grade air. Use the molecular weight of the compound to calculate the microliter amount to be spiked into the bag to achieve desired concentration. The spike amount is determined by using the following equation.

$$S = \frac{C * V * 24.46}{M * \left(1000\frac{ng}{\mu l}\right)}$$

S Spike amount required in order to obtain the desired concentration (µl)
C Desired concentration (ng/L)
V Volume of the Tedlar Bag (1L)
M Molecular Weight of the compound
24.46 Molar Volume of gas at 25°C, 1atm

Example:

Make a 100,000ng/L intermediate standard of Chloro-difluoromethane (Freon22) in a Tedlar Bag, where M=86

$$S = \frac{100{,}000\frac{ng}{L} * 1L * 24.46}{86 * \left(1000\frac{ng}{\mu l}\right)} = 28.44\mu l$$

9.2.2.2.4 *The Working standard* for extra compounds is prepared in a canister by spiking an aliquot of the intermediate standard (glass SDB or Tedlar bag) using a heated gastight syringe. The preparation of these standards shall follow the instructions detailed in Section 9.2.1.2. The concentrations for working standards are usually 20 and 200ng/L, however different concentrations can be chosen which work best for a particular project.

9.2.3 Initial Calibration Verification (ICV) - (Laboratory Control Sample - LCS) Prepare a secondary source standard (either a different manufacturer or different lot from the same manufacturer as the initial calibration standard) using the same procedures as the primary source. The ICV/LCS working standard should contain each target analyte present in the calibration working standard. Prepare the ICV/LCS working standard at a concentration of 200ng/L. Differing injection volumes account for the allowed concentrations listed in Table 4 for SCAN and 4A for SIM. The preparation of this standard shall follow the instructions detailed in Section 9.2.2, using the certified second-source standard cylinder.

9.2.4 Continuing Calibration Verification (CCV) Standard The CCV is the same as the initial calibration working standards detailed in Section 9.2.2.

9.2.5 Screening Standards Recommended procedure: Prepare a 0.5ug/mL and/or a 3.0ug/mL concentration standard so that the GC may be calibrated utilizing a few levels (may include approximately 0.5ng, 150ng and 600ng). However, other concentrations can be prepared depending on the desired range.

Any of the desired standard concentrations (primary and secondary) may change as long as the equations and the appropriate densities remain the same.

9.3 Storage and Expiration Dates

- All standards that are to be stored in a freezer shall be stored at ≤-10°C for DoD projects.

- Neat Stock Liquids are stored at < -10˚C (-10˚C to -20˚C) as specified by the manufacturer or for a period of five years.
- Equi-Mass Primary Stock Standard is a cocktail or soup of neat compounds (containing compounds in equal mass amounts) used to in preparing intermediate gas phase standards and shall be stored in the freezer at < -10˚C (-10˚C to -20˚C) for up to six months. This is assuming that the soup is sealed with a septum-containing screw cap or Mininert™ valve. The selection of the compounds for the soup should be performed in accordance with the guidelines in Volume 6.5 of the *Tekmar*-DOHRMANN Application Note.
- Purchased Stock Standards Cylinders must be stored at laboratory temperature for a period of 2 years or as specified by the manufacturer before vendor re-certification or purchase of new standards. Expiration dates of the cylinders must be entered into the yearly wall calendar located next to the cylinders. Analysts must verify that the assigned expiration dates of prepared standard canisters do not exceed the parent standard expiration date.
- Intermediate Calibration Standards prepared by static dilution must be stored in an oven at a temperature of approximately 60°C to ensure analyte vaporization. Every time a standard is prepared from the static dilution bottle (SDB), the concentration changes. To increase the useful lifetime of an SDB standard, remove volumes of 25mL or less. The volume removed can be manipulated by increasing the SDB concentration or by adjusting the canister final volume/pressure. Depending upon the volume removed, an SDB intermediate standard is stable for approximately two months as long as new working standards made from this standard continue to meet acceptance criteria. These bottles must be in the oven for a minimum of one hour prior to use in preparing working standards. The guidelines for the storage and expiration date for the intermediate calibration standards are stated in Volume 6.5 of the *Tekmar*-DOHRMANN Application Note.
- Prepared Stock / Intermediate Calibration Standards prepared in canisters (1000ng/L) may be stored at laboratory conditions for up to three months in an atmosphere free of potential contaminants. Upon preparation, canister standards should be allowed to sit for approximately 24 hours prior to use in order for equilibration to take place. Shorter equilibration periods may be necessary and acceptable as long as performance criteria are met.
- Calibration or Working Calibration Standards prepared in canisters may be stored at laboratory conditions for one month in an atmosphere free of potential contaminants. Upon preparation, canister standards should be allowed to sit for approximately 24 hours prior to use in order for equilibration to take place. Shorter equilibration periods may be necessary and acceptable as long as performance criteria are met.

10) Preventive Maintenance

10.1 A maintenance log will be kept documenting maintenance performed on each analytical system. The serial numbers of each instrument shall be recorded, and each log entry must include a description of the maintenance performed and be initialed by the analyst performing or observing/authorizing maintenance by an outside contractor.

The instrument maintenance log must be kept current. An entry shall be made in the appropriate log every time maintenance is performed (no matter the extent). The entry in the log must include.

(a) The date of maintenance
(b) Who did the maintenance
(c) Description of the maintenance
(d) Proof that the maintenance activity was successful

A notation of a successful tune and continuing calibration or initial calibration and the file number that accompanies the data will serve as proof that the maintenance is complete and the instrument is in working order.

The extent of the maintenance is not important, however, it is important that a notation be included for each maintenance activity such as changing a column, tuning the instrument, changing the pump oil, cleaning the source, ordering a part. In addition, a notation should be made in the logbook stating that no samples were analyzed during the days that the instrument was down and no active maintenance was being conducted (i.e., where no other notation was made in the logbook for those days).

10.2 Concentrating Trap

Routine maintenance includes periodic solvent cleaning of the Silco steel lines in the valve oven if contamination is suspected. Also, periodic replacement of the multi-sorbent or partial replacement of the trap if analyte specific deterioration is detected is required. See Attachment 5 for trap packing instructions. For specific trap information refer to the instrument maintenance logbook.

After repacking, the trap should be baked at 265°C for a minimum of three hours (or until a clean blank is generated) and a partial repacking requires baking (at 265°C) the trap for a minimum of 20 minutes (or until a clean blank is generated).

10.3 GC System

Column performance is monitored by observing both peak shapes and column bleed. Over time, the column will exhibit a poor overall performance, as contaminated sample matrices are analyzed. The length of time for this to occur will depend on the samples analyzed. When a noticeable decrease in column performance is evident and other maintenance options do not result in improvement, the column should be replaced (see Section 8.5). Whenever GC maintenance is performed, care should be taken to minimize the introduction of air or oxygen into the column.

Clipping off a small portion of the head of the column often improves chromatographic performance. When cutting off any portion of the column, make sure the cut is straight and “clean” (uniform, without fragmentation) by using the proper column-cutting tool. When removing any major portion of the column, which will affect the retention times and elution characteristics, a change in instrument conditions may be required to facilitate nominal analytical activity.

Declining performance can also be due to ineffective column ferrules, which should be replaced when a tight seal around the column is no longer possible. This can be detected with the use of a leak detector.

10.4 Mass Spectrometer

The Mass Selective Detector (MSD) ion source requires periodic cleaning to maintain proper performance. Symptoms of a dirty ion source include difficulty keeping the MSD

in tune and fluctuating internal standard areas. The vacuum system should be serviced every six months, including changing the pump oil and checking the molecular sieve in the back-streaming trap.

10.5 Instrument Tuning

The instrument is tuned with guidance from the procedure described in the HP Operations Manual, when necessary.

10.6 Computer Troubleshooting

Computer care and troubleshooting is conducted by the IT department. Refer to Section 8.6 for the computer hardware and software requirements.

Computers are selected to meet or exceed operating system and or acquisition software requirements. Periodic upgrades of memory are performed to maintain or improve system performance and reliability. Upgrades may be performed on systems until instrument hardware configurations become the limiting factor.

Basic Troubleshooting Outline:

1) Document occurrence and severity in IT Log
2) Interview user(s)
3) Investigate any available logs (Event Logs, Acquisition Logs, etc.)
4) Determine if problem is isolated (single user or acquisition) or widespread (multi user or network).
5) If multiple possibilities exist for cause, then eliminate in systematic manner.
6) Hardware issues are addressed with component replacement (beginning with most suspect portion).
7) Software issues are addressed first with internet investigation (user blogs, software source updates/findings).
8) Network issues are investigated from the Server, to Switch, to Network Card; utilizing all available managed devices to help discover possible failure points.
9) In some cases, system corruption may require reload or complete system replacement.
10) Finalize documentation in IT Log with actions taken
11) Perform periodic follow-up with User and review any log found to have suspect events that suggested source of issue.

11) Procedure

11.1 Initial Calibration

The initial calibration is performed to determine instrument sensitivity and the linearity of the GC/MS response for the target compounds.

Initial calibration requirements are as follows:

1. A minimum of 5 concentrations must be used to calculate the calibration curve.
2. An initial calibration must be performed at a minimum initially per instrument, annually thereafter or whenever the continuing calibration verification standard does not meet the acceptance criteria.
3. Highest concentration, together with the lowest concentration, defines the calibration range.
4. The method reporting limit for any reported analyte must be at >/= the lowest calibration point.
5. The initial calibration event may not be interrupted by maintenance.

6. Only one value per concentration may be used.
7. Analyze calibration standards from lowest to highest concentration.
8. All ICAL analyses must be completed within the 24-hour tune window.
9. If 5 calibration standards are in the ICAL, one standard may be re-analyzed. If 6 to 10 calibration standards are in the ICAL, two calibration standards may be re-analyzed.
10. One of the calibration points from the initial calibration curve must be at the same concentration as the continuing calibration verification standard.
11. The upper end of the calibration range must not exhibit any peak saturation for any analyte or the range must be lowered accordingly.
12. The initial calibration model must be linear calibration using average of response factors and cannot be changed for any reason.
13. Point dropping policy
    - Minimum of 5 consecutive concentrations must be used to calculate the calibration curve.
    - Lowest concentration must be at or below the MRL (LOQ) and may not be dropped unless the MRL is changed to the concentration of the remaining lowest standard.
    - Points at the high end may be dropped, but doing so lowers the calibration range.
    - Points may not be dropped from the interior of the curve unless an assignable cause (i.e., gross dilution error, missing internal standards, purge malfunction, standard preparation error, or instrument malfunction) is accounted for and documented. In these instances, all the analytes in that calibration standard must be dropped from the calibration curve as the corrective action (the reason must be documented and the results maintained with the documentation for the final ICAL).
    - Dropping individual compound points from the upper or lower end of the calibration range to improve linearity is not considered an error correction. The reason for dropping these points does not need to be documented but the ICAL documentation must state the revised calibration range if the MRL must be adjusted or the calibration range is lowered for a particular compound. This must be documented on the ICAL Review Checklist.

      When an individual compound point is dropped from an ICAL both the response and concentration fields in the compound database of the method must be cleared. This ensures the average ICAL RRF calculates correctly when executing the CCV check routine.

    - A calibration standard may be re-analyzed if the first analysis of the standard has been dropped and other requirements in this policy are met (i.e., still within 24 hours).
    - Once the ICAL has been used to calculate and report sample results it MUST not to be changed for any reason.
    - It is recommended that if an analyte has a higher MRL than the lowest concentration analyzed that the low standard be automatically dropped from the curve (i.e., acetone MRL is 5, drop at least the 0.4ng point).

11.1.1 Calibration Points Analyze the calibration standards (analyze low to high) that span the monitoring range of interest of the samples. For SCAN, the range is typically 0.5ng-100ng on column; however, 0.1ng on column may be added if low level analyses are requested. For SIM, the range is 20pg on column to 50,000pg on column. The dynamic range is dependent on the sensitivity of a

particular instrument as well as the required reporting limit for a given project and may be adjusted accordingly. Refer to Table 3 (SCAN) and Table 3A (SIM) for the concentrations of the compounds of interest in the initial calibration at each particular calibration concentration level.

Note: Refer to the EXCEL TO-15 Standard Concentration templates, located on the network at Q:\\TO15 Std. Concentrations\Std. Conc. Templates for both the SIM and SCAN templates. These templates must be utilized for the documentation of the standard canister concentration selection, final ICAL level concentrations and the determination of the correct injection volumes for the selected standard canister concentrations. If the primary or secondary stock standard cylinder concentrations are revised (upon re-certification or new purchases), the EXCEL spreadsheet templates, injection amounts and the ICAL concentrations in each instrument method must be adjusted accordingly. Other templates may be employed as long as they are validated and provide at least the same information.

SCAN

1. Determine if the lower end of the calibration range is to be 0.1ng or 0.5ng on column. If the low end is 0.1ng, then the 1ng/L standard must be utilized.
2. Determine if the 1ng/L or 20ng/L standard canister is to be used for the 0.5ng on column point.
3. Follow the instructions in the spreadsheet and save the file under the correct instrument folder and the initial calibration method identification.
4. Print the final ICAL concentration sheets and place into the corresponding ICAL folder

11.1.2 Recalibration Each GC/MS system must be recalibrated following any instrument maintenance which may change or effect the sensitivity or linearity of the instrument, if the continuing calibration verification acceptance criteria are not met and at least annually. The following procedure must be followed when updating an initial calibration method.

1. Open the most recent method.
2. Save the method with the new ICAL method ID using the "Save Method As" option. Date used in the method ID must be the date files were analyzed.
3. Quantitate midpoint standard and check retention times and integrations. Update retention times if necessary using QEdit or Easy ID (Tools → Easy ID). Requant if any changes are made and verify all peaks are identified correctly. Print.
   a. While midpoint standard is loaded update reference spectra (Continuing Calibration → Update Reference Spectra).
   b. With midpoint standard loaded update qualifier ion ratios and retention times (Initial Calibration → Update Levels → Select Update Level and then select Retention Times (Replace) and Replace Qualifier Ion Relative Responses).
   c. If necessary adjust integration parameters prior to processing remaining ICAL points.
4. Quantitate remaining ICAL standards. Review each peak for retention time, integration, and print. Review low level standards for acceptable signal to noise ratios and high level standards for saturation.
5. All responses must be cleared from ICAL before updating (Initial Calibration → Clear All Calibration Responses).

6. Update responses for each standard level (Initial Calibration → Update Levels) or (Initial Calibration → Quick Levels Update). If Quick Levels Update is used do not requant datafiles.
7. Save method.
8. Check Response Factor Report and evaluate whether any points should be dropped following the criteria outlined in this SOP.
9. Save method if any changes are made.
10. Verify calibration files listed on Response Factor Report are correct.
11. Verify file ID, acquisition time, quant time, update time, and last update information is correct on the Calibration Status Report.

11.1.3 Analytical Window If time remains in the tune window after meeting the acceptance criteria for the initial calibration, samples may be analyzed according to the procedure described in this document (see Section 11.5.2). If time does not remain in the analytical window, a new sequence shall commence with the analysis of the instrument performance check compound (BFB) and the continuing calibration verification standard.

11.1.4 Procedure The system should be operated using temperature and flow rate parameters equivalent to those in Section 11.6. Use the standard prepared in accordance with Section 9.2.2 of this SOP. Attach the calibration standard and internal standard/surrogate canisters to the designated inlets on the preconcentrator and open the canister valves. Analyzing different volume aliquots of the calibration standards produces differing concentrations.

Analyte responses (target ion areas) are tabulated and recorded using the Enviroquant program. Quantitation ions for the target compounds are shown in Table 2 and 2A and the primary ion should be used unless interferences are present, in which case the secondary ion may be used, but the reason documented in the initial calibration file and all subsequent quantitations utilizing that ICAL must be performed using the same ion selections. Refer to Section 13.2 for the required calculations and Section 12.4 for the acceptance criteria.

11.1.4.1 Additional Requirements The procedure for performing and generating a new initial calibration method must follow a few additional requirements.

1. If any analyte lacks the appropriate sensitivity (3 to 1 signal to noise ratio) at the low end of the calibration range, this point must be dropped from the curve and the MRL/LOQ raised accordingly.
2. No detector saturation may occur for any compound; the upper calibration level must produce no saturated peaks. Exhibited by:
   - The flattening of the response for the higher concentration standards as shown on the plot;
   - The presence of a reverse tail or rise on the front part of the peak;
   - The observed actual percent ratio of the secondary ion presence is lower than the expected percent ratio; or
   - The presence of a flat topped peak and again by the decline or saturation of the secondary ion compared with the expected % recovery.

11.1.4.2 LOQ Establishment, Verification and Acceptance Criteria

1. The LOQ must be set within the calibration range (≥ low std. of the current passing ICAL) prior to sample analysis.
2. The LOQ is verified by analyzing an LOQ verification QC sample containing the analyte at 1-2 times the claimed LOQ.
2. The LOQ for each analyte must be > the analyte's LOD.
3. The verification is acceptable if:
   a. The S/N ratio is at least 3:1 for each analyte.
   b. All ion abundances are acceptable per the requirements in this document.
   c. The % recovery for each analyte is within the laboratory generated control limits or 70-130% recovery for the annual Navy LOQ verification.
4. Using from 2 to 4 LOQ verification points, calculate the ongoing %RSD to demonstrate precision at the LOQ.
5. If the LOQ verification check fails, determine and document the cause. Additional LOQ verification checks must be performed at a higher level to set a higher LOQ.
6. Turn in all LOQ verification data (quantitation reports and software reports/checks) to QA regardless of pass or fail.
7. Verify the LOQ on each instrument quarterly. Navy accreditation requires an annual LOQ verification.

11.1.5 Initial Calibration Review Analyst's calculation and assessment along with a peer review of all ICAL data and documentation as stated in Attachment 2 is required before the ICAL may be used to analyze samples. In the case where samples are placed on the autosampler and allowed to run overnight, the sample results may only be reported if the ICAL is reviewed and found to be acceptable. The ICAL checklist in Attachment 2 must be used to document the review and approval process.

Perform a review of specific aspects of the calibration which might compromise data quality such as inappropriate extension of the calibration range with detector saturation and/or a lack of sensitivity for any analyte. Analyte concentrations which do not meet the signal to noise ratio or exhibit saturation are not to be reported and must be eliminated from the initial calibration. These instances should be followed by a short explanation regarding the reason for the omission.

11.1.6 Initial Calibration File An ICAL file is to be created for each initial calibration performed per instrument into which is placed the following ICAL documents. The file shall remain in the laboratory and be filed by instrument and date.

- ICAL Checklist filled out, reviewed and approved
- BFB tune analysis report
- Calibration status report (aka Calibration History)
- Relative Response Factor Report / Percent Relative Standard Deviation
- Quantitation report for each calibration standard (including manual integration documentation – before and after manual integration)
- ICV quantitation report and % recovery report.
- TO-15 Standard Concentration Spreadsheet (exact ICAL level concentrations and ICV concentrations)
- Any manual integration documentation

11.2 Initial Calibration Verification Standard

Verify the initial calibration by analyzing an initial calibration verification standard (ICV). This standard shall be obtained or prepared from materials acquired from a different manufacturer or lot from that of the initial calibration and prepared according to Section 9.2.3.

Analyze 50ng or less (refer to Table 4 for the secondary source standard concentrations) of the ICV standard depending on the dynamic range of a given instrument and refer to Section 13.4 for the required calculations.

11.3 Sample Preparation

The pressure/vacuum is checked and the canister pressurized upon receipt by the laboratory, as needed. When necessary, canisters shall be pressurized with humidified zero grade air. However, if the samples are to be analyzed in accordance with EPA Method 3C then the samples must be pressurized with UHP Helium (refer to Section 11.11 for additional information). The client must be made aware of this in advance and given the option of either submitting two canisters for analysis or receiving a report with qualified results (TO-15 Modified).

Depending on the size of the canister and location of sampling and as specified in the SOP below, samples may be pressurized to approximately 1.0psig to 3.5psig. Additional information may be found in the *SOP for Evaluation and Pressurization of Specially Prepared Stainless Steel Canisters*. Initial and final pressures are recorded in LIMS and should be repeated on the back of the sample tag. The dilution factor created by filling the sample canister is calculated using equation number 12 in Section 13.7.

11.4 Screening

The analyst must screen a sample or subset of samples if the source is of unknown origin. Typically, if the source is known to be indoor or ambient outdoor air, no screening is necessary. However, if screening is required make sure that the instrument is calibrated. A single point calibration is sufficient; however, the instrument may be calibrated utilizing a two point calibration. The ICAL points are recommended to be at approximately 0.5ng, 150ng and/or 600ng spanning the desired dynamic range. Refer to Section 9.2.5 for additional information.

Inject a 1mL or smaller aliquot of each sample into a GC/flame ionization detector (FID) system that has been calibrated with a standard containing a subset of the target analytes. This subset represents the most commonly found compounds in air samples, such as acetone, trichloroethylene, and toluene. Use the results to determine the maximum volume of sample to be analyzed by TO-15 by utilizing the following equation. Dilutions may be prepared as necessary according to Section 11.11.1.

$$I = \frac{C}{H}$$

Where:

I Injection volume (mL)
C Maximum calibration level (ng on column)
H Compound screening concentration (ng/mL)

Example: Select the compound with the highest concentration (toluene = 1.0ng/mL). If the upper calibration level is 100ng on column, then the following calculation determines the maximum injection volume to analyze.

$$\frac{100ng}{1.0ng/mL} = 100mL \text{ maximum injection volume}$$

11.5 Analytical Sequence and Data System Setup

11.5.1 Data System For the Tekmar AUTOCAN, fill in the sequence log of the Teklink program with the appropriate information. Refer to the Section 11.6.1 for the operating parameters.

For HP Chemstation, load the appropriate acquisition method for the GC/MS in the top window of the Chemstation program. Suggested GC/MS operating parameters are given in Section 11.6.2.

11.5.2 Analytical Sequence The analytical sequence must be completed for the analysis of ≤20 field samples. Re-runs, dilutions, and sample duplicates are not counted as separate samples. A method blank (MB) shall be run to monitor for laboratory introduced contamination. There must be at a minimum a laboratory duplicate (LD) analyzed in each batch to assess batch precision. The following generalized analytical sequence is to be followed:

Analytical Sequence Guideline

With Calibration	Tune Check[1] Calibration Standards (5 Standards Minimum) ICV Standard[2] (Acts as the ICV and LCS) QC Canister Checks[6] MB[7] Sample(s) – 1-20 Laboratory Duplicate[4]
With Continuing	Tune Check[1] CCV Standard[5] QC Canister Checks[6] MB[7] LCS[3] MRL Check Standard[8] Sample(s) – 1-20 Laboratory Duplicate[4]

[1] The instrument performance check solution must be analyzed initially and once per 24 hour (or as specified by the project) time period (sequence / tune window) of operation. All analyses for a sequence must be initiated (injected) prior to the expiration of the tune window.

[2] In this scenario, the ICV may also be evaluated as the LCS (differing acceptance criteria).

[3] An LCS shall be analyzed at a rate of 1 in 20 or fewer samples. The LCS is the second source calibration check standard analyzed at the lower end of the calibration curve (below the midpoint).

[4] A laboratory duplicate must be analyzed at a rate of 1 per 20 or fewer samples. The duplicate must be rotated among clients, whenever possible. Also, a duplicate laboratory control sample may be analyzed to assess precision to meet project requirements or due to sample matrix effects.
[5] A CCV must be analyzed at the beginning of every analytical sequence.
[6] Any number of QC check canisters may be analyzed in the sequence to determine a canister cleaning batch or batches acceptability.
[7] Any of the QC Check Canisters may serve as the method blank as long as the minimum requirements detailed in this document are met. A method blank shall be analyzed at a rate of 1 in 20 or fewer samples.
[8] A MRL check standard may be analyzed with each batch of 20 or fewer samples (when an initial calibration is not analyzed within the same batch). Additional information is included in Section 11.17.

Note: Client project batch specifications may require certain modifications to the analytical sequence; however, a batch may not be more lenient than that which is specified in this document.

11.6 Conditions

11.6.1 Sample Collection Conditions The suggested settings and system parameters are as follows:

Adsorbent Trap

Set Point:	35˚
Sample Volume:	up to 1L
Dry Purge:	300mL
Sampling Rate:	100mL/min (utilize for a sample injection volume of >100mL); 40mL/min (utilize for a sample injection volume of 25-100mL)
Desorb Temp.:	200˚C to 230˚C
Desorb Flow Rate:	8-10mL/min He, measured at refocuser split vent
Desorb Time:	3.0 minutes

Refocusing Trap

Temperature:	-180˚C
Injection Temp.:	160˚C
Injection Time:	1.0 min

Adsorbent Trap Reconditioning Conditions

Temperature:	265°C
Initial Bakeout:	3 hours or until clean blank is obtained
After each run:	5-8 minutes

Sample Run Time

Each analytical run is approximately 20 minutes long; the total cycle time is about 30 minutes between injections.

11.6.2 GC/MS System

Optimize GC conditions for compound separation and sensitivity.

Item	Condition
Carrier Gas	Helium
Flow Rate	1.0-1.6mL/minute
Temperature Program	Initial Temperature: ~20˚C Initial Hold Temperature: 3 minutes Ramp Rate: 5˚C/min to 80˚C 2nd Ramp: 10˚C/min to 160˚C 3rd Ramp: 20˚C/min to 240˚C for 5 min hold
Detector B (MSD *Interface)*	260˚C
Electron Energy	70 Volts (nominal)
Mass Range (Scan mode)	34 to 280 amu
Mass Range (SIM mode)	Scan masses corresponding to the target analytes
Scan Time	To give at least 10 scans per peak, not to exceed 1 second per scan.

Note: *The instrument may be operated in Selective Ion Monitoring (SIM) mode if requested by the client.*

11.7 Instrument Performance Check

Since the BFB tuning compound is included in the internal standard and surrogate standard canister and an autosampler is used, it is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to the reduction and approval of any data collection. The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or continuing calibration verification criteria) begins at the injection of the BFB, which shall be documented in laboratory records. Upon completion of the successful BFB tune, the tune report must be printed and retained on file for future reference.

The mass spectrum of BFB must be acquired in the following manner.

- Inject 50ng or less (on column)
- Three scans (peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged.
- Background subtraction is conducted using a single scan prior to the elution of BFB.
- All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.
- The ion abundance criteria must not be changed from the requirement stated in this document (TO-15 or TO-14A, as requested).

All subsequent standards, samples and QC samples associated with a BFB analysis must use identical instrument conditions.

11.8 Continuing Calibration Verification Standard

Verify the calibration each working day, where necessary (e.g., an ICAL was not analyzed or the tune window has closed) by analyzing a continuing calibration verification (CCV) standard from the initial calibration standard canister. The concentration of the calibration verification may be varied between the low calibration standard and the

midpoint of the calibration range; however, the concentration must be at one of the levels analyzed in the initial calibration. Refer to Table 3 for the standard concentrations. Refer to Section 13.3 for the required calculations.

DoD QSM Requirement: A CCV standard must be analyzed daily before sample analysis; after every 24 hours of analysis time; and at the end of the analytical batch run.

11.9 Canister Quality Control Check and Method Blank

The method blank must be a sample of a matrix similar to the batch of associated samples that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure, and in which no target or interferences are present at concentrations that impact the analytical results for sample analyses. Prepare a canister that has not left the building by pressuring with humidified zero air. Analyze an aliquot of one liter along with the same volume of internal standard and surrogate as standards and samples. Additionally, a blank must be analyzed whenever a high concentration sample is encountered and carryover is suspected. For all method blanks the unique laboratory barcode for the canister must be included in the sample analysis identification.

A Quality Control (QC) check canister pressurized with humidified zero air may serve as a method blank as long as the analyte concentration requirements stated in the canister quality control check section (Sections 12.7 and 12.8) and other requirements (refer to Section 12.12 for internal standard requirements) are met. Assuming continuing failure, another QC canister or a new canister must be prepared and analyzed in order to verify that no system contamination exists. For tracking purposes the unique laboratory barcode given to a canister shall be the information included in the sample analysis identification.

11.9.1 Sampling Systems Section 7.1 and 8.4 of Method TO-15 describe the setup and certification procedure for a specific sampling apparatus that has been used by the EPA for several of its large air monitoring programs. These systems are rarely used for the types of projects that make up the bulk of the laboratory's work. The vast majority of samples analyzed by the laboratory are taken into canisters either as grab samples or using a simple time integrated sampling device (flow controller), as in Section 8.2.1 of the method, so these procedures are not part of the typical protocol for providing sampling materials to clients. The laboratory has developed an SOP for the cleaning and certification of the materials it provides its clients for obtaining air samples to be analyzed by method TO-15. Refer to the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters* for additional information.

It is this laboratory's interpretation that the sampler system certification procedure described in Section 8.4.4 of the TO-15 method applies to the specific sampling apparatus described in the method and not to the sampling procedures used by our clients. The laboratory does not maintain a dynamic calibration manifold or canister sampler apparatus as described in the method and thus performance of the relative accuracy certification procedure described in section 8.4.4 is not possible.

11.10 Laboratory Control Sample

The laboratory control sample is a sample matrix, which is free from the analytes of interest and spiked with a standard containing known amounts of analytes. The laboratory control sample is an injection of the initial calibration verification standard. Inject the LCS (ICV) at concentrations below the midpoint of the calibration curve. Make

sure that all of the pertinent information is included on the quantitation report including the sample identification (LCS), concentration, standard used, and analyst.

11.11 Sample Analysis

Prior to analysis, all sample containers (canisters and bags) should be at temperature equilibrium with the laboratory.

- Attach sample canisters to Tekmar AUTOCan using a 9/16" wrench. Bottle Vacs use a proprietary quick connect fitting (Micro-QT, Entech Instruments). Tedlar bags can be connected using soft silicone tubing or a 3/16" fitting with a reusable ferrule.
- Before opening the valve, check for leaking fittings by running the leak check program in the Teklink software. Quick connect fittings must be leak checked before connecting the sample container.
- If system is leak tight, open the canister valves and start the automated preconcentration procedure. Make sure the Chemstation data acquisition software has been readied.
- Maintain the trap at an elevated temperature until the beginning of the next analysis.

Check all target compounds using the QEdit routine in Enviroquant, making sure all extracted ion chromatogram peaks are integrated properly (see Section 11.15).

Note 1: The secondary ion quantitation is only allowed if there is sample matrix interference with the primary ion. If the secondary ion quantitation is performed, document the reasons in the instrument run logbook and/or on the quantitation report (initial and date any notation).

Note 2: Each female Micro-QT fitting must be purged after use to remove any remaining sample residue and prevent contamination from subsequent usage. Connect a male Micro-QT fitting to a source of ultrapure or carbon-filtered gas. Adjust the pressure to about 10 psig using an inline regulator. Connect the female fitting for several seconds, then remove and place in an oven kept at 60ºC until the next use. Do not heat the fitting higher than 80ºC.

SCAN Mode - The instrument is normally operated in the SCAN mode, where the following procedure may be followed.

- Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic range from 34 to 270 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning allows identification of unknown compounds in the sample through searching of library spectra. See operating conditions in Section 11.6.
- Generate a quantitation report for each run.
- If reporting Tentatively Identified Compounds (TICs), refer to Section 11.11.2 for identification criteria.

SIM Mode - When the client requests SIM mode, select SIM instead of SCAN mode and identify a minimum of two ions per analyte of interest. Also, a minimum of two ions for each internal standard and surrogate compound should be selected.

Helium Pressurization – If a canister is pressurized with helium, a correction factor is applied to sample volumes extracted from the canister via auto sampler. This is due to the difference in thermal properties between helium and air. A correction factor worksheet has been generated to determine the exact volume taken from a canister and may be found at J:\\A-GCMS\Helium Pressurization. Save file, print the sheet and include with the data. Refer to the instruction page in the template for all of the instructions and calculations including backfilled canisters.

AutoCAN Leak Checks – Canisters should be put on at least two different AutoCAN positions to confirm a "leak". In addition, the valve threads should be inspected for defects which may prevent a good seal with the AutoCAN. Once a canister has "failed" the leak check it must be tagged, an NCAR initiated, and the PM notified. Regardless of what the client or PM specifies as the fate of the sample, the canister must be put on maintenance hold to complete a full 24-hour leak check. The leaking canister must be documented on the Sample Review Checklist (or yellow sheet). This is a fixed QA procedure with no allowance for deviation.

11.11.1 Sample Dilution If any target analyte results are above the highest level of the initial calibration, a smaller sample aliquot should be analyzed. The dynamic range of volume aliquots for the automatic cryogenic concentrator is 15ml to 1L. If a volume smaller than 15ml is to be analyzed, a dilution should be made in a Tedlar bag, or the sample directly injected using a gastight syringe. Guidance in performing dilutions and exceptions to this requirement are given below.

- Refer to Section 11.6.1 (Adsorbent Trap Sampling Rate) for the required sampling rate if less than 100mL is to be analyzed.
- Use results of the original analysis to determine the approximate dilution factor required and get the largest analyte peak within the initial calibration range.
- The dilution factor must be documented (and included in the final report) and chosen in such a way as to keep the response of the analyte peak for a reported target compound in the upper half of the initial calibration range of the instrument.

Tedlar bag dilution:

- Make a dilution by filling a Tedlar bag with 1.0 liter of humidified zero air using a one-liter gas syringe.
- Calculate the volume of balance gas needed to obtain the required dilution.
- Remove the difference in the balance gas using a syringe.
- Add the calculated sample amount using a gastight syringe.

Direct injection:

- Make a direct injection by attaching a clean, humidified zero air filled canister to the preconcentrator autosampler using 1/4" stainless steel or teflon tubing with a "tee" septum port. This canister should be the same canister that may be used as the method blank.
- Inject the sample through the septum while the preconcentrator withdraws a 200cc aliquot from the canister.

11.11.2 Tentatively Identified Compounds When requested, a mass spectral library search may be made for the purpose of tentatively identifying sample components not associated with the calibration standards. The necessity to

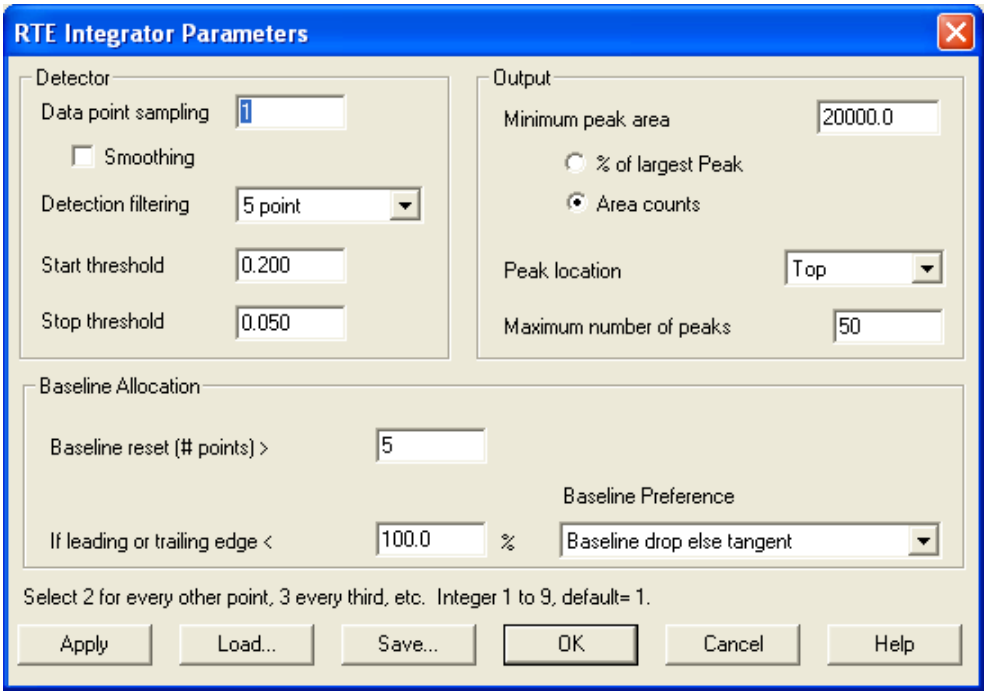
perform this type of identification will be determined by the purpose of the analyses being conducted. Data system mass spectral library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

Certain programs may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. The following guidelines are used for making tentative identifications.

- Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ±20%. For example, for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance should be between 30 and 70%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library reduction programs can sometimes create these discrepancies.
- The concentration of the tentatively identified compound is estimated by assuming a response factor of 1.0 and comparing the response of the tentatively identified compound to the response of the nearest internal standard.
- If non-target analytes are not Q-deleted from the quant report, the analyst must evaluate whether these compounds should be reported as TICS.

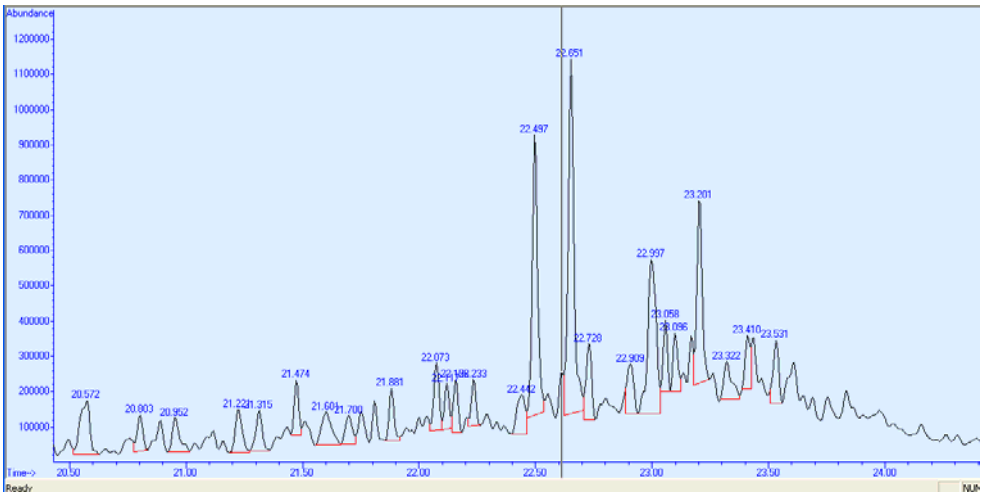
<u>Procedure for Reporting Tentatively Identified Compounds (TICs) for samples and associated Method Blanks</u>

1. Load the datafile in the main Enviroquant window.
2. Load the TIC integration parameters (LSCINT.p). Typical setpoints are as shown below.

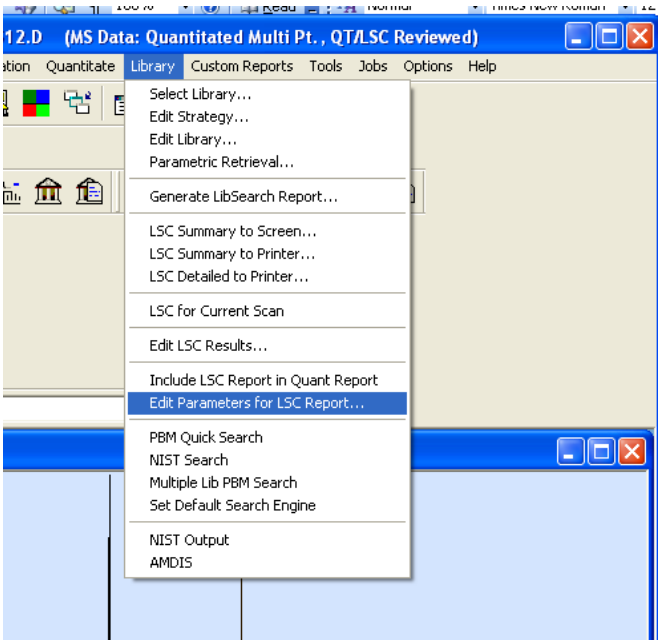


3. Integrate the chromatogram and inspect the peak integrations. Adjust the parameters as needed to achieve integration that will:

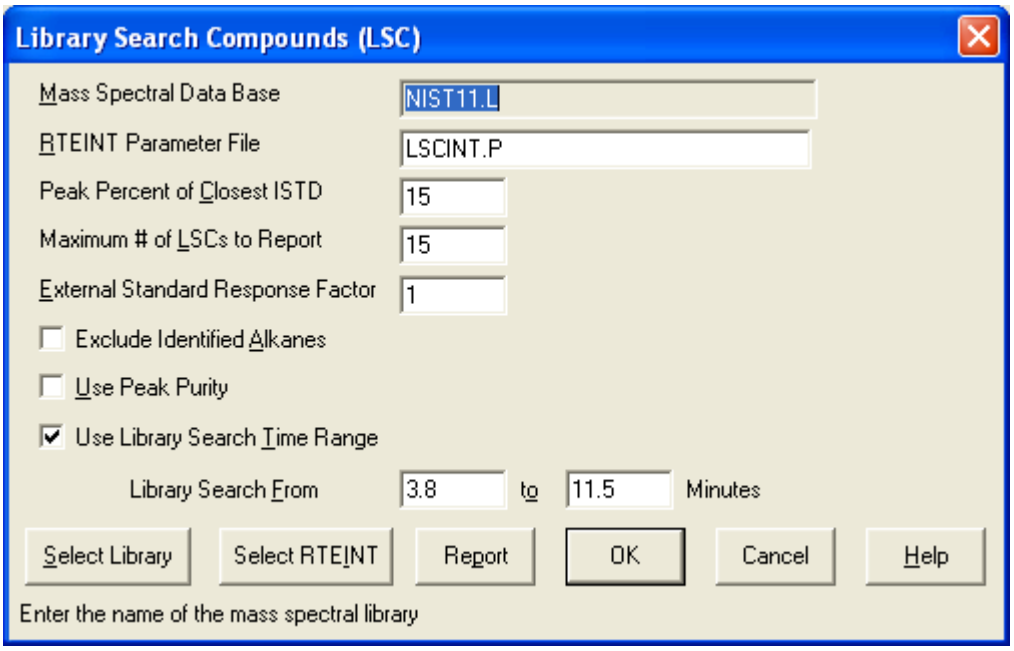
   - Resolve closely-eluting peaks that only have a small valley separating them.
   - Not include excess area below the peak in a complex matrix with an elevated baseline.
   - Include peak tailing when necessary.
   - Yield a sufficient number of peaks that will ensure that the internal standards are included.



4. Edit the parameters to be used in generation the library search report:



Select the most current mass spectral library database available, the correct integration parameters file, the area threshold (as a percent of IS area), number of peaks to report, and a time range of the chromatogram to search (set to start after the CO2 peak).



5. Run the LSC routine from the Library menu. You may choose 'LSC Summary to Screen' (Calculate/Generate Report) to get a quick view of the results and then proceed if they seem acceptable. Set the default printer to 'Adobe PDF' and then choose 'LSC Detailed to Printer'.
6. Open the pdf file and inspect the LSC summary (last page). Check the internal standard areas and confirm that they are correct. If any IS area is biased high due to a coeluting peak use the 'Edit LSC Results' routine to switch all associated TICs to use a different IS. If all three IS peaks have coelutions substitute the areas from the daily method blank in the calculations.
7. Use the LSC Summary as a guide and inspect the chromatogram in the data analysis window. Integrate the chromatogram from the Integrate menu and look for peaks that may have been missed by the LSC routine. Possible reasons for missed peaks are excessive tailing (organic acids), RT close to a target compound, coeluting peaks with no valley between them. These will need to be added manually.
8. Use the DOSCAN routine from the Tools menu to search individual missed peaks one by one. This will add them to the LSC list.
9. Go back into the Edit LSC Results routine and make any necessary changes to compound names and/or the internal standard used for quantitation.
10. Run the macro "QT '0,0,C' by clicking the Custom Tool 1 button. This will update the LSC list to the quant.csv file.
11. Run the LSC Detailed to Printer routine from the Library menu (Generate Report *only*). This will print the file to pdf.
12. Excel Reporting
    1. In Excel, open the TIC reporting template (I:\A-GCMS\TICS\System\StarLIMS_TICQ).
    2. Enter the service request number and click ok.
    3. Click the Get Samples button. Select the samples to be reported. Delete any samples that are not to be reported (right click/delete row).
    4. Click the Update PEF button.
    5. Click the Get TICs from CSV button. Enter the date analyzed and select the instrument ID.
    6. Click the Apply to all Samples button. Change the date for any sample that was analyzed on a different date.
    7. Click the Apply Instrument to all Samples button.
    8. Enter file number in column E (i.e. enter 07 for file 12301507.d).
    9. Click the Copy Data button. This copies the TIC info to the report sheets.

11.12 Duplicate

A duplicate must be analyzed to assess laboratory precision and samples selected for duplicate analysis shall be rotated among client samples, where applicable. Some projects or sample matrix issues may require the analysis of a duplicate laboratory control sample (DLCS).

11.13 Internal Standard (IS)

The concentration of internal standard added to each standard, field sample and QC sample must be consistent from that of each current ICAL standard.

11.14 Surrogates

Internal standards/surrogates must be added at the same volume for every standard, sample and QC sample. Surrogate compound recoveries are requested by a number of clients, but are more appropriately used as system monitoring compounds. This is due to the fact that the compounds are introduced directly into the analytical system and not into the canisters or bags. It is for this reason that they are not considered to be true surrogates and a fixed window is applied. Additionally, surrogates are not included in the ICAL because they are not required by the method and are only system monitoring compounds.

11.15 Manual Integration and Q Deletion

A list of abbreviations (codes) that may be used to give a reason for performing either of these procedures are listed in the *SOP for Data Review and Reporting*.

11.15.1 Manual Integration The integration for each peak must be legally defensible and shall be checked to ensure that it has been integrated properly and consistently between samples, standards and QC samples. All peak reviews and manual integrations must follow the requirements specified in the *SOP for Manual Integration Policy* and the *SOP for Laboratory Ethics and Data Integrity.* The requirements in the above stated procedure include when manual integrations are performed, raw data records shall include a complete audit trail for those manipulations (i.e., chromatograms showing both the integration prior to any manual integrations and those depicting the corresponding manually integrated peaks), and notation of rationale, date, and initials of person performing the manual integration operation. In addition, manual integrations must be reviewed and approved by a second reviewer and the manual integrations maintained in the appropriate job file.

Reporting Requirements Certain project requirements including samples which are submitted under the Department of Defense (DoD) QSM require that the case narrative include an identification of samples and analytes for which manual integration is required. Refer to project requirements to determine if this is necessary.

11.15.2 Q Deletion Q deleting may be performed to either delete a false positive or delete non-target compounds.

11.16 Detection Limits and Limits of Detection

The MDL shall be performed in accordance with the procedure outlined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation.* The detection limit shall be used to determine the LOD for each analyte.

11.16.1 Performance and Acceptance Criteria

1. The MDL must be <0.5ppbV for each analyte (Method 11.11.1).
2. Following the MDL study perform a Limit of Detection (LOD) verification on all instruments (performing this method). Spike the LOD at 2-4x the MDL; the spike level establishes the LOD.
3. LOD Acceptance
   - Analyte must be detected reliably and identified by the method-specific criteria (i.e, ion confirmation) and produce a signal that is at least 3 times the instrument's noise level (3:1 signal to noise ratio).
   - It is specific to each combination of analyte, matrix, method and instrument configuration.

- The LOD must be verified quarterly on each instrument (spiked at LOD) using the criteria listed above.

4. If the LOD verification fails (per #3), repeat the detection limit determination and LOD verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration.
5. The laboratory shall maintain documentation for all detection limit determinations and LOD verifications (regardless of pass or fail).

11.17 Method Reporting Limit Check Standard

It is recommended to analyze a MRL check standard at the current MRL or required MRL for the batch (per client requirements) of twenty or fewer samples if the CCV fails low for any target compound. A MRL check standard may also be required per client specifications.

This check standard can also serve as the LOQ verification if it meets the specific requirements listed in Section 11.1.4.2. Apply the requirements and retain all documentation accordingly. Refer to Attachment 4 for Minnesota specified MRL check standard criteria.

11.18 Method Modifications

Method modifications are not allowed under TNI standards; therefore, a statement, however worded, must be included in the final report indicating that data reported does not fall under the laboratory's NELAP certificate of approval. In addition, the following items are considered to be method modifications and must be reported accordingly.

- Sample collection in gas collection bags
- The pressurization of canisters with nitrogen or helium (if EPA Method 3C is requested) refer to Section 11.11.

12) Quality Control Requirements and Corrective Action

12.1 To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.2 Corrective actions shall follow the procedures outlined in the *SOP for Nonconformance and Corrective Action*, where appropriate. Any maintenance which may alter instrument sensitivity or linearity must result in the re-analysis of the entire sequence including the tune compound, ICAL or CCV or any batch QC.

12.3 Instrument Performance Check

12.3.1 Acceptance Criteria

Refer to Tables 1 and 1A for the required ion abundance criteria.

12.3.2 Corrective Action Perform auto tune or manual tune and then re-analyze BFB. If the BFB acceptance criteria are still not met, the MS must be retuned according to the procedure outlined in the instrument user's manual. Perform necessary maintenance and make notations in the instrument maintenance logbook. It may be necessary to clean the ion source, or quadrupole, or take other necessary actions to achieve the acceptance criteria. An acceptable tune is required for sample results to be calculated and reported.

12.4 Initial Calibration

12.4.1 Acceptance Criteria Refer to the following acceptance criteria for the initial calibration.

- The RRT for each target compound at each calibration level must be within 0.06RRT units of the mean RRT for the compound.
- The calculated %RSD for the RRF for each compound in the calibration standard must be less than 30% with at most two exceptions up to a limit of 40% (this may not be true for all projects).

  DoD QSM/Navy Requirement: The two exceptions of %RSD up to 40%, allowed by the method, are not allowed.

- For each Internal Standard the area response (Y) at each calibration level must be within 40% of the mean area response $\overline{Y}$ over the initial calibration range.
- The retention time shift for each of the internal standards at each calibration level must be within 20s of the mean retention time over the initial calibration range for each internal standard.

  Navy Requirement: The absolute retention time for each of the internal standard and calibrated analytes must be within ±0.20 minutes (12 seconds) of the mean retention time for the corresponding internal standard or analyte over the initial calibration range.

- All of the following information must be retained to permit reconstruction of the initial instrument calibration: calibration date, test method, instrument, analysis date, analyte identification, analyst's initials, concentration and responses, and response factors.
- All initial instrument calibrations must be verified with an acceptable ICV.

12.4.2 Corrective Action Follow the initial calibration requirements detailed in Section 11.1 for information on re-analyzing or dropping points and the restriction of maintenance performed during the analysis of the initial calibration standards.

If the initial calibration results are outside the established acceptance criteria, corrective actions must be performed and all associated samples reanalyzed, if reanalysis of the samples is not possible, data associated with an unacceptable initial calibration shall be reported as estimated with the appropriate data qualifiers.

12.5 Initial Calibration Verification Standard (ICV)

12.5.1 Acceptance Criteria The percent recovery for each compound in the ICV must be between 70%-130% for all analytes except vinyl acetate, which must be within 50-150%. Exceptions to this allowance for the vinyl acetate recovery are project specific requirements and any DoD type project, which shall adhere to the 70-130% requirement for all target compounds.

12.5.2 Corrective Action If the initial calibration verification technical acceptance criteria are not met, reanalyze and if it fails again, prepare a new canister and analyze. If the criteria are still not met inspect the system for possible sources and perform any necessary maintenance and make a notation in the maintenance logbook of any steps taken. It may be necessary to clean the ion source or change the column. Perform a new initial calibration if any performed maintenance has altered instrument linearity and/or sensitivity. Perform another

initial calibration or if reanalysis is not possible, data associated with an unacceptable ICAL/ICV shall be reported as estimated with the appropriate data qualifiers.

12.6 Continuing Calibration Verification (CCV)

12.6.1 Acceptance Criteria All compounds must be evaluated prior to rounding. The percent difference for each target analyte must be within plus or minus 30% of the initial calibration average RRFs.

12.6.2 Corrective Action If the continuing calibration verification technical acceptance criteria are not met, reanalyze and if it fails again, prepare a new canister and analyze. If the criteria are still not met inspect the system for possible sources of the problem and perform any necessary maintenance and make a notation in the maintenance logbook of any steps taken. It may be necessary to clean the ion source or change the column.

If any corrective action and/or reanalysis fails to produce continuing calibration verification within acceptance criteria (analyzed immediately following the initial failure), then either two consecutive successful verifications must be performed following corrective action or a new initial calibration must be performed; however, refer to 16.6.2.1 below.

DOD Requirement: If a CCV fails, the laboratory must immediately analyze two additional consecutive CCVs (The two consecutive CCVs must be analyzed within one hour).

- Both of these CCVs must meet acceptance criteria in order for samples to be reported without reanalysis.
- If either of these two CCVs fail or if the laboratory cannot immediately analyze two CCVs, the associated samples cannot be reported and must be reanalyzed.
- Corrective action(s) and recalibration must occur if the above scenario fails.
- Flagging data for a failed CCV is only appropriate when the affected samples cannot be reanalyzed. The laboratory must notify the client prior to reporting data associated with a failed CCV.

12.6.2.1 Method Reporting Limit Check Standard

If a per batch MRL check standard is analyzed due to a failing CCV or client requirement and is unacceptable for any compound (sensitivity; ratio or %D), reanalyze at the same or higher level within the same batch and report data with the CCV flag and case narrative notes accordingly. Reporting data with these conditions must be acceptable per project and client requirements otherwise corrective action must be initiated and samples reanalyzed.

Refer to Section 11.1.4.2 for annual (NELAP and Navy) and quarterly (DoD) LOQ verification requirements.

12.7 Canister Quality Control Check

The actual cleaning procedure, number of cans to select for analysis (to release a cleaning batch) and corrective actions are covered in the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters* and are not covered in this section. However, the procedure for analyzing and certifying a cleaning

batch is included. If a canister passes as a QC canister it meets all of the requirements for a method blank (Method, TNI Standards, and Department of Defense Quality Systems Manual – DoD QSM, etc.).

12.7.1 Scan Analyses A canister is considered "clean" for normal SCAN analyses if the analysis shows <0.2ppbv of any target analyte (analyte exceptions listed in table below). If a canister passes as a QC canister it meets all of the requirements for a method blank (Method, TNI Standards, and Department of Defense Quality Systems Manual - DoD QSM, etc.).

Low Level SCAN Analyses For those analytes with a MRL of 0.1ug/m3, the QC criteria of <MRL is acceptable; otherwise, <0.2ppbV is required (analyte exceptions listed in table below).

SIM Analyses Results <MRL will be acceptable as this complies with the <0.2ppbV method requirement.

DoD QSM Requirement Each canister must be individually certified. A canister is considered clean if no reported analytes are detected at >1/2 the LOQ.

ANALYTE EXCEPTION LIST					
Compounds	ppbV	On Column (ng)	Compounds	ppbV	On Column (ng)
Target Analytes	0.2	0.50	Acrylonitrile	0.2	0.43
Chloromethane	0.2	0.41	Acetone	1.5	3.5
1,3-Butadiene	0.2	0.44	Ethanol	1.9	3.5
Acetonitrile	0.2	0.33	Vinyl acetate	0.99	3.5
Acrolein	0.65	1.5	1-Butanol	0.23	0.70
Isopropanol	0.28	0.70	Carbon Disulfide	1.1	3.5
2-Butanone	1.2	3.5			

Document the status of the check in LIMS and return the canister to the canister conditioning room. Additionally, if the check was found to be acceptable, the quantitation report must be kept on file for future reference

12.7.2 Tentatively Identified Compounds (TIC) If the batch of canisters are to be used for tentatively identified compounds (TIC) analysis, any non-target peaks present in the QC check canister analysis must be evaluated and determined to be less than the TIC reporting limit (10% of the internal standard). The concentration is estimated by assuming a RRF of 1.0 and comparing the response of the TIC to the response of the nearest internal standard.

12.8 Method Blank

12.8.1 Acceptance Criteria

- The concentration of a targeted analyte in the blank cannot be at or above the MRL, AND be greater than 1/10 of the amount measured in any associated sample. For any project that requires reported results less than the MRL, all associated measurements found in the MB should result in a qualifier; however, project requirements may differ and must be followed. Refer to DoD requirements listed below.

- The method blank should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.
- For DoD samples, the method blank will be considered to be contaminated if:

  1. The concentration of any target analyte in the blank exceeds 1/2 the reporting limit or is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater);
  2. The concentration of any common laboratory contaminant (acetone, ethanol, carbon disulfide, and methylene chloride) in the blank exceeds the reporting limit and is greater than 1/10 the amount measured in any sample or 1/10 the regulatory limit (whichever is greater); or
  3. The blank result otherwise affects the samples results as per the test method requirements or the project-specific objectives.

The laboratory shall evaluate whether reprocessing of the samples is necessary based on the above criteria.

12.8.2 Corrective Action If the analyte concentration results in the blank do not meet the acceptance criteria repeat analysis with remaining QC canisters until results are acceptable or prepare a canister per Section 11.9. If the analyte results in the blank still do not meet the acceptance criteria the source of the problem must be investigated and measures taken to eliminate the source. Each method blank must be critically evaluated as to the nature of the interference and the effect on the analysis of each sample within the batch. Determine whether the contamination is from the instrument or due to contamination in the blank container (if results from the new can are not acceptable then the system is probably contaminated). In all cases, the corrective action (reprocessing or data qualifying codes) must be documented. However, the specific corrective action depends on the type of project the blank is utilized for; therefore, refer (below) to the reporting/reprocessing requirements.

DEPARTMENT OF DEFENSE (DoD) QSM PROJECT: Any sample associated with a blank that fails the criteria shall be reprocessed in the same or subsequent analytical batch, except when the sample analysis resulted in a non-detect. If reanalysis is not performed, the results shall be reported with appropriate data qualifier.

OTHER PROJECT TYPE: Appropriate corrective measures must be taken and documented before sample analysis proceeds. However, if this is not a possibility and the results must be reported follow the reporting requirements stated in Section 16.4.

12.9 Laboratory Control Sample (LCS)

12.9.1 Acceptance Criteria Round all results to the nearest whole number prior to determining if the acceptance criteria have been met. The percent recoveries must be within the laboratory-generated limits and are referenced in the electronic TO-15 Method Manual. However, Arizona requires the percent recovery for each compound in the LCS to be 70%-130% (to match the ICV requirement). Therefore, the ICV exception for vinyl acetate stated in Section 12.5 requires the percent recovery for AZ samples to be 50-150%.

Note: Client project requirements and DoD requirements shall take precedence over the AZ requirement for AZ samples. Meaning if a sample is collected for a

DoD project in AZ, DoD requirements specified in this document and the project specific QAPP (if supplied) are to be followed.

DoD Requirement: In the absence of client specified LCS reporting criteria, the LCS control limits outlined in the DoD QSM Appendix C tables shall be used when reporting data for DoD projects.

12.9.2 Corrective Action If the LCS criteria are not met, determine whether the cause is instrumentation or the result of a poor injection. If the problem is instrumentation, perform maintenance and if the problem is with the injection re-analyze the LCS. DoD considers the same analyte exceeding the LCS control limits two out of three consecutive LCS to be indicative of non-random behavior; therefore, this trend should be monitored and the appropriate corrective action taken when it occurs.

12.10 Sample Results

12.10.1 Acceptance Criteria

- Sample results must be quantitated from the initial instrument calibration and may not be quantitated from any continuing instrument calibration verification.
- The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, initial calibration verification technical acceptance criteria described in this document.
- All target analyte peaks must be within the initial calibration range, diluted or reported with the appropriate data qualifier.

12.10.2 Corrective Action

- If the retention time for any internal standard within the sample changes by more than 20 sec from the latest daily calibration or initial calibration mid-point standard, the GC/MS system must be inspected for malfunctions, and maintenance performed as required. Repeat sample analysis as needed.

  Navy Requirement: The absolute retention time for each of the internal standard and calibration analytes must be within ±0.20 minutes (12 seconds) of the mean retention time for the corresponding internal standard or analyte over the initial calibration range.

- If the area for any internal standard changes by more than ±40 percent between the sample and the most recent calibration, check for possible matrix interferences and re-analyze at a greater dilution. If the requirement is still not met and matrix interference is not detected the GC/MS system must be inspected for malfunction and maintenance made where necessary.
- When corrective actions are made, samples analyzed while the instrument was not functioning properly must be re-analyzed or the appropriate data qualifiers must be attached to the results.

  To the extent possible, samples shall be reported only if all of the quality control measures are acceptable. If a quality control measure is found to be out of control, and the data must be reported, all samples associated with the out of control quality control measure shall be reported with the appropriate data qualifier(s).

12.11 Laboratory Duplicate

12.11.1 Acceptance Criteria The relative percent difference must fall within ±25%. This RPD criterion also applies to duplicate laboratory control samples (DLCS).

12.11.2 Corrective Action If the duplicate results do not meet the technical acceptance criteria, perform another duplicate analysis. If the results are still unacceptable and the associated samples are not reanalyzed then all of the sample results in the associated batch must be flagged accordingly.

12.12 Internal Standards

12.12.1 Acceptance Criteria The following acceptance criteria must be applied to each run (except the ICAL – see Section 12.4).

- The area response for each internal standard in the blank must be within ±40 percent of the area response for each internal standard in the most recent valid calibration. (CCV or mid-point from the initial calibration, whichever is most current).
- The retention time for each internal standard must be within ±0.33 minutes of the retention time for each internal standard in the most recent valid calibration. (CCV or mid-point from the initial calibration, whichever is most current).

  Navy Requirement: The absolute retention time for each of the internal standard and calibration analytes must be within ±0.20 minutes (12 seconds) of the mean retention time for the corresponding internal standard or analyte over the initial calibration range.

12.12.2 Corrective Action

- Internal Standard Responses If the problem is with the instrument, perform maintenance. If the problem is with a sample, check for interferences. If the response is high, it is likely that interference is present. In this case, lower the volume or aliquot of the sample and re-analyze. If the problem persists, report the results with the best quality and qualify the results. If the problem is corrected with the lower volume analysis, report those results.
- Internal Standard Retention Times If the retention time for any internal standard within the sample changes by more than 20 sec from the latest daily calibration or initial calibration mid-point standard, the GC/MS system must be inspected for malfunctions, and maintenance performed as required. Repeat sample analysis where required.

12.13 Surrogates

12.13.1 Acceptance Criteria Since the matrix precludes the use of true surrogates and there is no established method criterion, acceptable surrogate recoveries are based on a fixed window of 70 - 130%. This is the typical requirement from clients. Additionally, these limits are referenced in SW-846 for use as guidance in evaluating recoveries. These limits are sufficient for evaluating the effect indicated for the individual sample results.

12.13.2 Corrective Action Poor surrogate recovery should be followed by re-analyzing a smaller aliquot to mitigate any matrix interferences. Evaluate the out of control surrogate for the effect on individual sample results.

12.14 Method Reporting Limit Check Standard

12.14.1 Acceptance Criteria Per client requirements or if the CCV is biased low for any compound, then evaluate the MRL check standard. Analyte must be detected reliably and identified by the method-specific criteria (i.e, ion confirmation) and produce a signal that is at least 3 times the instrument's noise level (3:1 signal to noise ratio). A percent difference +/-50% is recommended but program and client specific requirements must be followed if applicable.

12.15 Sample Holding Time Expired

The customer is to be notified that the sample's holding time was missed and the customer is to decide if the sample analysis is to continue. The documentation of missed holding time and the client's decision to proceed must be included in the corresponding job file. A statement dictating all holding time occurrences must accompany the sample results in the final report.

13) Data Reduction and Reporting

13.1 This method has specific requirements including the use of canisters; any modification must be reported accordingly. All reports that fall under the laboratory's certificate of approval (in accordance with TNI standards) must include a statement(s) clarifying any deviations from the scope of this certification. Refer to Section 13.10 for additional information and specific items, which require this clarification.

13.2 Initial Calibration

Tabulate each of the following:

13.2.1 Equation Number 1 - **Relative Response Factor (RRF):**

$$RRF = \frac{A_x C_{is}}{A_{is} C_x}$$ where:

A_x is the area response of the analyte quantitation ion.
A_{is} is the area response of the corresponding internal standard quantitation ion.
C_{is} Internal standard concentration, ng.
C_x Analyte concentration, ng.

Note: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC samples is the same from run to run.

13.2.2 Equation Number 2 - **Average (or Mean) RRF:**

$$\overline{RRF} = \frac{\sum_{i=1}^{N} RRF_i}{N}$$ where:

RRF_i are the individual RRFs from each concentration level in the initial calibration curve.

N is the number of calibration concentration levels.

13.2.3 Equation Number 3 - **Standard Deviation, SD:**

$$SD = \sqrt{\sum_{i=1}^{N} \frac{\left(RRF_i - \overline{RRF}\right)^2}{N-1}}$$ where:

RRF_i are the individual RRFs from each concentration level in the initial calibration curve.

$\overline{RRF}$ Average (or Mean) RRF of all concentration levels in the initial calibration curve.

N total number of calibration concentration levels

13.2.4 Equation Number 4 - **Percent Relative Standard Deviation, %RSD:**

$$\%RSD = \frac{SD}{\overline{RRF}}(100)$$ where:

SD Standard Deviation calculated in equation number 3

$\overline{RRF}$ Average or Mean RRF

13.2.5 Equation Number 5 - **Relative Retention Time (RRT):**

$$RRT = \frac{RT_C}{RT_{is}}$$ where:

RT_C Retention time of the target compound, seconds.

RT_{is} Retention time of the internal standard, seconds.

13.2.6 Equation Number 6 - **Mean Relative Retention Time ($\overline{RRT}$):**

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT_i}{n}$$ where:

$\overline{RRT}$ Mean relative retention time (seconds) for the target compound for all initial calibration levels.

RRT_i Relative retention time for the target compound in level i.

n Number of calibration levels

13.2.7 Equation Number 7 - **Mean Area Response ($\overline{Y}$):**

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$ where:

Y_i Area response for the primary quantitation ion for the internal standard for each initial calibration standard.
n number of calibration concentration levels

13.2.8 Equation Number 8 - **Mean Retention Times ($\overline{RT}$):**

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$ where:

$\overline{RT}$ Mean retention time, seconds
RT_i Retention time for the internal standard for each initial calibration standard, seconds.
n number of initial calibration levels

13.3 Continuing Calibration Verification

- Calculate the (RRF) of each target compound using equation number 1.

13.3.1 Equation Number 9 - **Percent Difference, %D:**

$$\%D = \frac{RRFx - \overline{RRF}}{\overline{RRF}}(100)$$ where, for any given analyte:

RRF_x is the RRF from the CCV being evaluated.
$\overline{RRF}$ is the mean RRF from the current calibration curve.

13.4 Percent Recovery – ICV, LCS, Surrogates, MRL Check Standard

13.4.1 Equation Number 10 - **Percent Recovery (%R):**

%R = X/TV x 100

where
X = Concentration of the analyte recovered
TV = True value of amount spiked

13.5 Duplicate Analysis

13.5.1 Equation Number 11 - **Relative Percent Difference (RPD):**

$$\frac{x_1 - x_2}{\bar{x}}(100)$$ where:

x_1 First measurement value
x_2 Second measurement value
$\bar{x}$ Average of the two values

13.6 Internal Standards (IS)

- Calculate the mean area response $\overline{Y}$ for each internal standard using equation number 7.
- Calculate the mean of the retention times for each internal standard using equation number 8.

13.7 Pressure Dilution Factor (PDF)

13.7.1 Equation Number 12 - **PDF**, for samples collected in canisters:

$$PDF = \frac{P_{atm} + P_f}{P_{atm} + P_i}$$ where:

P_{atm} is the ambient atmospheric pressure, 14.7 psi at sea level.
P_f is the final sample canister pressure, in psig.
P_i is the initial sample canister pressure, in psig. This will most often be a negative value (sub-ambient initial pressure).

13.8 Results

If a canister has been pressurized with Helium and the Tekmar AutoCan was utilized, refer to Section 11.11.

13.8.1 Equation Number 13 - For calculating analyte concentrations in a sample, the starting point is the nanogram amount generated by the HP Enviroquant software, which appears on the quantitation report.

$$ng_x = \frac{A_x ng_{is}}{A_{is}\overline{RRF}}$$ where:

ng_x is the nanogram amount of analyte *x*.
A_x is the area response of the analyte's quantitation ion.
A_{is} is the area response of the corresponding internal standard's quantitation ion.
ng_{is} is the internal standard amount, in nanograms.
$\overline{RRF}$ is the average or mean RRFs

13.8.2 Equation Number 14 - The final analyte concentration, C_x, in units of micrograms per cubic meter (µg/m³), is then calculated from the following:

$$C_x = \left(\frac{ng_x PDF}{V}\right)\left(\frac{1\mu g}{1000 ng}\right)\left(\frac{1000 l}{1 m^3}\right)$$ where:

V is the sample volume analyzed, in liters.
PDF is the sample canister pressure dilution factor.

13.8.3 Equation Number 15 - To convert to units of parts per billion volume (ppbv):

$$ppbv = \frac{\mu g/m^3}{MW} x 24.46 \qquad \mu g/m^3 = \frac{ppbv}{24.46} xMW$$ where:

MW is the molecular weight (Table 2) of the analyte, in g/mole.
24.46 is the molar volume of an ideal gas at 298 K (25 °C) and 760 mmHg (1 atm), in liters per mole (l/mol).

C_x the final analyte concentration in micrograms per cubic meter.

13.8.4 Equation Number 16 – Helium Pressurization (Injection Amount)

Applicable to canisters pressurized with helium and injected utilizing the mass flow controller of the AutoCAN. For full instructions and calculations, refer to the 1st tab of the template located at: J:\A-GCMS\Helium Pressurization\System\HE Pressurization Template.

13.9 Data Review

The analyst must review data on a real time basis for all calibration and QC data. The QC data must be evaluated by analytical sequence following the Daily QC review checklist (Attachment 3). The data shall be reviewed and the sample results calculated and assessed by one analyst and reviewed by a second qualified analyst. The Sample Review checklist (Attachment 3) is used to document sample review per service request and once completed, initialed and dated must be filed with each job file.

Initial calibrations must be reviewed in the same manner as QC data with all ICAL documentation retained in a separate file organized by instrument and date. Refer to the initial calibration checklist in Attachment 2 for the review guideline. The ICAL file must contain all the pertinent information stated in Section 11.1.6.

13.10 Reporting

The results of each test shall be reported clearly, unambiguously and objectively, and shall include all the information necessary for the interpretation of the test results and information required by this laboratory's policy, TNI standards, DoD Manual (applicable version, see reference section), client projects, and the TO-15 method including modifications, observances, data qualifiers, and certification information.

If the project requires that results be reported below the MRL (LOQ), but above the LOD all of the requirements specified for normal reporting apply (3:1 S/N ratio and ion abundance). This is regardless of the fact that the results will be qualified as estimated.

13.10.1 Analysis Observations / Case Narrative Summary Form

This form, which is included in the *SOP for Laboratory Storage, Analysis and Tracking*, may be generated when there are specific sample composition information or analysis issues and/or observations. In addition, during the analysis, specific identification information or problems, interferences, calibration issues, flags, and additional/expanded explanation of flags should be added to the form. This form may be modified as long as the sections and basic concepts are reserved. All data qualifiers and flags should follow those

listed in the most recent Quality Assurance Manual or as defined in any client requirements.

This form may be used as a means for documentation. This form, among other information, will be reviewed when compiling the final report and case narrative. Alternatively, information may be included on the Daily QC and Sample Review Checklists (Attachment 3). All information regarding the job shall remain in the file, in order that sufficient documentation is available to recreate the job from sample receipt through analysis, data reduction, and reporting.

13.10.2 NELAP\TNI Requirements

The following items do not comply with TNI standard requirements and must be reported accordingly. A statement, however worded, must be included in the final report indicating that data reported does not fall under the laboratory's NELAP certificate of approval.

- Reporting any compound which is not included in the second source standard (ICV or LCS) does not meet NELAP requirements.
- In addition, a report that contains a compound not included on the NELAP certificate of approval must also include the statement listed above.

13.10.2.1 Modifications

Method modifications are also not allowed under TNI standards; therefore, a statement, however worded, must be included in the final report indicating that data reported does not fall under the laboratory's NELAP certificate of approval. In addition, the following items are considered to be method modifications and must be reported accordingly.

- Sample collection in gas collection bags
- The pressurization of canisters with nitrogen or helium (if EPA Method 3C is requested) refer to Section 11.11.

13.10.3 Surrogates

Only report surrogates at the request of the client. If any surrogate is out of control, all samples results (with surrogates requested) associated with the surrogate must be reported with the appropriate data qualifier.

13.10.4 DoD Requirements

Report results with the appropriate data qualifiers, if samples cannot be reanalyzed for any reason. In addition and at a minimum, the following situations are to be noted in the case narrative: manual integrations, CCV out of control, and results exceeding the calibration range.

13.11 Storing Electronic Data

The initial calibration data must be stored in a quantitation method (on the server) using a unique filename and may not be overwritten at any time in order to maintain an accurate audit trail. There are multiple quantitation methods, which are subsets of the compound list in Table 2. Therefore, files will be named with a notation indicating the compound list and the date of the corresponding initial calibration. In addition, all data files including method blanks, continuing calibration verification, laboratory control samples and client submitted samples files are saved in a unique sub-directory on the server.

13.12 Sufficient raw data records must be retained on file of all laboratory analyses described in this document including passing QC canister checks, tune checks, instrument calibrations, verifications, sample analyses and dilutions, QC checks, and method detection limit studies. The information that is required includes: analysis/calibration date and time, test method, instrument, sample identification, analyte identification, analyst's initials, concentrations and responses, as well as standards used for the analysis and calibrations, all manual calculations including sample dilutions and manual integrations to permit reconstruction of analyses. Information entered and reported on the quantitation report and instrument run log must be complete and accurate. All data shall be obtained following defensible and ethical practices in accordance with the most recent Quality Assurance Manual and the *SOP for Laboratory Ethics and Data Integrity*.

Note: All data records must explicitly connect data to the initial instrument calibration. This includes all samples, continuing calibrations and QC samples.

13.13 The essential information to be associated with analysis, such as computer data files, run logs, etc. shall include: Sample ID code, date and time (if the holding time is 72 hours) of analysis, instrument operating conditions/parameters (or reference to such data), analysis type, all manual calculations including dilutions and manual integrations, analyst's initials, sample preparation (pressure readings and balance gas if pressurized with helium), standard and reagent origin, receipt, preparation, and use, as well as calibration criteria, frequency and acceptance criteria, data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions.

14) Method Performance

14.1 An on-going assessment of method performance is conducted in order to ensure that the laboratory is capable of reporting results which are acceptable for its intended use. Validation of the method is confirmed by the examination and provision of objective evidence that these requirements are met.

14.2 Method Detection Limit (MDL)

The procedure used to determine the method detection limits are as stated in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as defined in the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation*. The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is distinguishable from method blank results. The MDL concentrations are listed in Tables 2 and 2A for both SCAN and SIM modes and were obtained using spiked canisters prepared with humidified zero air, making at least seven replicate measurements of the compounds of interest, computing the standard deviation, and multiplying this value by the appropriate Student's t value for 99 percent confidence. Additionally, at least seven method blank results were processed according to the procedure described in this document. Refer to the *SOP for Performing Method Detection Limit Studies and Establishing Limits of Detection and Quantitation* for the method blank MDL calculation and additional requirements for establishing the MDL. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects. All MDLs, regardless of the mode of operation, meet the method performance criteria of <0.5ppbV.

14.3 Accuracy and Precision

Refer to Section 11.4 in the referenced method for information on replicate precision criteria for method performance. Single laboratory accuracy is presented as the second source initial calibration verification standard, which meets the method performance

criteria of 30%. Additionally, laboratory generated control limit data for LCSs are presented for the analytes of interest and may be referenced in the electronic TO-15 Method Manual. Refer to Section 11.1.4.2 for the accuracy and precision requirements for concentrations at the LOQ/MRL.

14.4 Selectivity

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification.

It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak must be acquired. Scanning also allows identification of unknown compounds in the sample by searching through library spectra.

The sample analysis using the GC/MS is based in part on a combination of retention times and relative abundances of selected ions. The retention time of each chromatographic peak should be ±0.10 minutes of the library/reference retention time of the compound. The acceptance level for relative abundance should be set at ±20% of the expected abundance. The data should be manually examined by the analyst to determine the reason for the # flag [(#) = qualifier out of range], if present and whether the compound should be reported as found or if there is matrix interference. A background subtraction may aid in this determination. Manual inspection of the qualitative results should also be performed to verify concentrations outside the expected range.

Specific selectivity information is provided in this section and document (such as relative retention time) as well as in the referenced method. Refer to the method for additional information on selectivity.

- Use NIST Library 2011 or newer version
- The *reference spectra updates* must be performed with every new ICAL utilizing the mid-level standard (minimum). If needed, the reference spectra may be updated sooner with the continuing calibration standard.
- *Retention time updates* must be performed using EasyID and not by updating to the method (InitCal \ Update Calibration). Refer to the Help selection of the software.

14.5 Demonstration of Capability

This laboratory has continuously performed this method since before July 1999. Therefore, ongoing demonstration of capable shall be performed and documented; however, the initial demonstration of method capability is not required.

14.6 Proficiency Testing (PT) Program

The laboratory shall participate in an air and emissions PT study for TO-15. The testing shall be performed in accordance with this document and meet the frequency and proficiency requirements detailed in the DoD QSM.

Proficiency testing samples including all accredited compounds are not available. Therefore, in addition to third party PT samples, intra laboratory comparisons must be

performed biannually to meet the DoD QSM proficiency testing requirements. Eight QC analyses from various analysts and instruments shall be compiled and statistical validity evaluated using a Z-score.

15) Pollution Prevention and Waste Management

15.1 All waste disposals shall be carried out in accordance with the requirements detailed in the *SOP for Waste Disposal.* In addition, canisters must be cleaned in accordance with the requirements detailed in the *SOP for Cleaning and Certification of Summa Canisters and Other Specially Prepared Canisters.*

16) Contingencies for Handling Out-of-Control or Unacceptable Data

16.1 The following is specific information on how to report unacceptable data. If the data requires a data qualifier flag, as specified in this SOP, refer to Appendix D of the most recent version of the Quality Assurance Manual for the appropriate data qualifier.

16.2 Initial Calibration and/or Initial Calibration Verification

All results reported with an unacceptable ICAL must be reported as estimated and all data shall be reported using defined qualifiers or flags or explained in the case narrative accordingly.

16.3 Continuing Calibration Verification

All results associated with an unacceptable CCV (other than #1 below) must be reported with the appropriate data qualifier, flag and/or explained in the case narrative.

1. When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples that are non-detects, then those non-detects may be reported without a qualifier.
2. When the acceptance criteria for the continuing calibration verification are exceeded high, i.e., high bias, and there are associated samples with detects, then those detects must be reported with a qualifier, flag and/or explained in the case narrative.
3. If however, the acceptance criteria for the continuing calibration verification are exceeded low, i.e., low bias, and there are associated samples that are non-detects, then those non-detects must be reported with qualifiers, flags and/or explained in the case narrative as having less certainty. However, along with the data qualifiers, the case narrative may include information stating the fact that the results were not significantly affected if:
   a. *An MRL check standard was analyzed and found to be acceptable. The MRL must be the same as that analyzed in the MRL check standard for those analytes that were biased low in the CCV. Adjust MRLs (if required), flag data and state the certainty in the case narrative where the sensitivity of the instrument was demonstrated at the MRL; therefore, results were not significantly affected.*
   b. *With the reporting limit adjusted to the next level in the calibration curve (typically 5 times higher) to prove the nonexistence of a false negative and note procedure in case narrative.*
4. If the acceptance criteria was exceeded (biased high) for the CCV and there were detectable results in a sample, the results may be "qualified" if the results exceeded the regulatory/decision limit (this is to be stated in the case narrative along with the data qualifiers or flags).
5. Data associated with a biased low CCV may be fully useable if the results reported exceed a maximum regulatory limit/decision level.

16.4 Method Blank

- If an analyte in the blank is found to be out of control and the analyte is also found in associated samples, those sample results shall be "flagged" in the report and the method blank results reported.
- If the analyte is found in the blank but not in the sample then the results for the sample may be reported without a qualifier.

16.5 Laboratory Control Sample

All results associated with an out of control laboratory control sample must be reported with the appropriate data qualifier. An indication of whether the LCS was out high or low should also be included.

16.6 Surrogate

Report sample results with the appropriate data qualifier.

16.7 Laboratory Duplicate

All batch sample results associated with an out of control laboratory duplicate must be flagged with the appropriate data qualifier.

16.8 Internal Standard

All target analytes associated with an out of control internal standard must be flagged with the appropriate data qualifier.

16.9 Estimated Sample Results

16.9.1 Sample Hold Time All occurrences of missed holding times must be included on the final report including those samples received and/or analyzed outside of the specified hold times detailed in this SOP.

16.9.2 Matrix Interference Sample data associated with matrix interference must be flagged with the appropriate data qualifier.

16.9.3 Results Outside Initial Calibration Range All sample results not bracketed by initial calibration standards (within calibration range) must be reported as having less certainty by reporting with the appropriate data qualifier.

17) Training

17.1 Demonstration of Capability

All analysts must be trained in accordance with the guidelines detailed in the *SOP for Training Policy*. Demonstrations shall also be performed in accordance with the TNI Standards and DoD Quality Systems Manual. Attachment 1 shall be used to document the training plan for new analysts' initial demonstration. Additionally, these demonstrations are performed anytime there is a change in instrument type, personnel or method.

Once performance is found to be acceptable, a required certification statement must be completed by the QA Manager and either the immediate supervisor or Laboratory Manager and retained on file as a demonstration of compliance.

17.1.1 Quarterly Demonstration A demonstration of method sensitivity must be performed *quarterly on each instrument* performing this method.

1) A spike at the current LOD must be analyzed.

2) Verification of precision and bias at the LOQ must be performed.

Refer to Section 11.1.4.2 (LOQ) and 12.14.1 (LOD) for additional information on how these demonstrations are to be performed as well as the acceptance criteria.

17.1.2 Annual Demonstration Each analyst must perform a demonstration of capability initially and annually. For the initial demonstration analyze four LCS standards at 1-4x the MRL (LOQ) either concurrently or over a period of days as a verification of precision and bias of the quantitation range. The standard deviation (n-1) and average percent recovery of the four replicates are compared against the method requirement for precision (±25%) and current laboratory control limits for bias/LCS.

17.1.3 Change in Personnel, Instruments, Method and/or Matrix The requirements in Sections 17.1.1 and 17.1.2 must be performed per the schedule noted and when there is a change in personnel, instruments, method or matrix. "Change" refers to any change in personnel, instrument, test method, or sample matrix that potentially affects the precision and bias, sensitivity, or selectivity of the output (e.g., a change in the detector, column type, matrix, or other components of the sample analytical system, or a method revision).

All completed attempts at this demonstration must be turned into the QA department for retention.

18) Summary of Changes

Table 18.1 Summary of Revision Changes

Revision Number	Effective Date	Document Editor	Description of Changes
25.0	08/18/2018	C. Arend	Applied updated SOP formatting style to first two pages and header/footer. Sections renamed and reorganized to align with *SOP for Preparing Standard Operating Procedures*. Section references updated throughout.
			1.1 – second paragraph - removed reference to Note 1 (note previously removed from SOP
			5.1 – removed "Summa" from section heading
			6 – removed table and sections and replaced with new sections 6.1 – 6.6
			6.1 – removed reference to Environmental Health and Safety Manual as document is being spilt into multiple documents
			7.1 – changed "stainless steel pressure vessel" to "passivated stainless steel canister"
			7.4 – last sentence – minor revision to wording
			8.9 – added last two bullets; removed "Summa" from first bullet
			9.2.1.3 – changed "Summa canister" to "canister"
			9.2.1.3.1 – added six month expiration when prepared in 30L or greater canister; changed "Summa canister" to "canister"
			9.2.2 – changed "Summa canister" to "canister" throughout

			9.2.2.1 - changed "Summa canister" to "canister" throughout
			9.2.2.2.4 – changed "Summa canister" to "canister"
			10.2 – removed reference to electronic method manual
			10.2.1.2 – changed "Summa canister" to "canister" throughout
			10.2.2.1 – changed "Summa canister" to "canister"
			10.3 – changed "Summa canister" to "canister"
			11.1.1 – revised low points of ranges
			11.5.2 – changed "Sample(s) – 1-19" to "Sample(s) – 1-20" since sample duplicate does not count as a separate sample. Revised first two sentences to add clarification.
			11.8 – changed "DoD QSM 5.1" to "DoD QSM"
			11.9.1 – changed "Summa canister" to "canister"
			12.4.1 – 4th bullet – added Nay specific requirement; changed "DoD QSM 5.1" to "DoD QSM"
			12.7.1 – changed "DoD QSM 5.1" to "DoD QSM"
			12.9 – minor revision to AutoCAN Leak Checks box
			12.9.1 – Direct Injection box – changed "Summa canister" to "canister"; removed "AFFCEE"
			12.10.2 – included Navy requirement
			12.12.1 – included Navy requirement
			Information previously in section 13 removed – redundant to information covered in section 12
			13.7.1 – changed "Summa canister" to "canister"
			13.11 – removed "eight-character" naming convention requirement
			14.2 – updated MDL procedure
			Information previously in section 17 removed – redundant to information covered in administrative SOPs
			17.1 – removed reference to specific section in TNI Standard
			19.5 – added 2016 TNI Standards
			19.7 – updated
			Table 2 – updated MDLs and MRLs
			Table 2A – updated MRL for 1,2,4-Trichlorobenzene; added Bromobenzene
			Table 3 – updated
			Table 3A – updated; added Bromobenzene
			Table 4 – updated
			Table 4A – updated; added Bromobenzene
			Attachment 3 – Sample Review Checklist – removed questions 3 and 4 from APH section

19) References and Related Documents

19.1 EPA Method TO-14A, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA/625/R-96/010b, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1997.

19.2 EPA Method TO-15, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA/625/R-96/010b, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1997.

19.3 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, January 1999.

19.4 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Addendum, January 17, 2002.

19.5 2009 TNI Standards; 2016 TNI Standards

19.6 *Preparation of Gas Phase Standards for Ambient Air Analysis,* Tekmar-DOHRMANN Application Note, Spring 96, Vol. 6.5.

19.7 DoD/DoE Quality Systems Manual Version 5.1, 2017; and Version 5.1.1, 2018.

19.8 Arizona Administrative Code, Title 9. Health Services, Chapter 14. Department of Health Services Laboratories, October 1, 2016.

19.9 Florida Department of Environmental Protection, Chapter 62-160.

19.10 Minnesota Department of Health, 4740.2065, *Standard Operating Procedures*, Statutory Authority: MS s 144.97; 144.98; History: 31 SR 446, Posted: October 09, 2006, Revised April 16, 2010.

20) Attachments

20.1 Tables

Table 1: Instrument Tune Check Ion Abundance Criteria (TO-15)

Table 1A: Instrument Tune Check Ion Abundance Criteria (TO-14A)

Table 2: Volatile Organic Compounds, EPA Compendium Method TO-15 (SCAN)

Table 2A: Volatile Organic Compounds, EPA Compendium Method TO-15 (SIM)

Table 3: Standard Concentrations (SCAN) (Primary Sources)

Table 3A: Standard Concentrations (SIM) (Primary Sources)

Table 4: Standard Concentrations (SCAN) (Secondary Sources)

Table 4A: Standard Concentrations (SIM) (Secondary Sources)

20.2 Attachments

Attachment 1 – Training Plan

Attachment 2 – Initial Calibration Checklist

Attachment 3 – Daily QC and Sample Review Checklists

Attachment 4 – State and Project Specific Requirements

Attachment 5 – Tekmar AutoCan Trap Packing Instructions

TABLE 1

Required BFB Key Ions and
Ion Abundance Criteria for Method TO-15

Mass	Ion Abundance Criteria[1]
50	8.0 to 40.0 percent of m/e 95
75	30.0 to 66.0 percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/e 95
173	Less than 2.0 Percent of m/e 174
174	50.0 to 120.0 Percent of m/e 95
175	4.0 to 9.0 Percent of m/e 174
176	93.0 to 101.0 Percent of m/e 174
177	5.0 to 9.0 Percent of m/e 176

[1] All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 1A

Required BFB Key Ions and
Ion Abundance Criteria for Method TO-14A

Mass	Ion Abundance Criteria
50	15 to 40 percent of m/e 95
75	30 to 60 percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5 to 9 Percent of m/e 95
173	Less than 2 Percent of m/e 174
174	>50 Percent of m/e 95
175	5 to 9 Percent of m/e 174
176	>95 and <101 Percent of m/e 174
177	5 to 9 Percent of m/e 176

Note: The criteria listed in Tables 1 and 1A shall be met or exceeded in order for EPA Compendium Methods TO-15 or TO-14A to be referenced.

TABLE 2 - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	**CAS Number**	**Molecular Weight**	**Density**	**Primary Ion[2]**	**Secondary Ion(s)[2]**	**MRL[3] (µg/m³)**	**MDL[3] (µg/m³)**	**IS[4]**
Bromochloromethane (IS1)	74-97-5	-	-	130	128, 132	-	-	-
Propene	115-07-1	42.08	NA	42	39,41	0.52	0.13	IS1
Dichlorodifluoromethane (CFC 12)	75-71-8	120.9	1.329	85	87, 101, 103	0.52	0.087	IS1
Chloromethane	74-87-3	50.49	0.911	50	52	0.50	0.086	IS1
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	76-14-2	170.9	1.455	135	137	0.51	0.084	IS1
Vinyl Chloride	75-01-4	62.50	0.9106	62	64	0.52	0.057	IS1
1,3-Butadiene	106-99-0	54.09	0.6149	54	39, 53	0.53	0.088	IS1
Bromomethane	74-83-9	94.94	1.6755	94	96	0.50	0.074	IS1
Chloroethane	75-00-3	64.52	0.8902	64	66	0.51	0.066	IS1
Ethanol	64-17-5	46.07	0.7893	45	46	5.3	0.37	IS1
Acetonitrile	75-05-8	41.05	0.7857	41	40	0.53	0.13	IS1
Acrolein	107-02-8	56.06	0.840	56	55	2.1	0.15	IS1
Acetone	67-64-1	58.08	0.7845	58	43	5.3	1.2	IS1
Trichlorofluoromethane	75-69-4	137.4	NA	101	103	0.53	0.081	IS1
Isopropyl Alcohol	67-63-0	60.10	0.7809	45	43	5.3	0.22	IS1
Acrylonitrile	107-13-1	53.06	0.8060	53	52	0.53	0.11	IS1
1,1-Dichloroethene	75-35-4	96.94	1.213	96	61	0.53	0.074	IS1
tert-Butanol	75-65-0	74.12	0.7887	59	57,41,43	1.1	0.16	IS1
Methylene Chloride	75-09-2	84.94	1.3266	84	49	0.53	0.15	IS1
Allyl Chloride	107-05-1	76.53	0.9376	41	76	0.53	0.072	IS1
Trichlorotrifluoroethane	76-13-1	187.38	1.5635	151	101	0.53	0.076	IS1

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	**CAS Number**	**Molecular Weight**	**Density**	**Primary Ion[2]**	**Secondary Ion(s)[2]**	**MRL[3] (µg/m³)**	**MDL[3] (µg/m³)**	**IS[4]**
Carbon Disulfide	75-15-0	76.14	1.2632	76	78	5.3	0.16	IS1
trans-1,2-Dichloroethene	156-60-5	96.94	1.2565	61	96	0.54	0.074	IS1
1,1-Dichloroethane	75-34-3	98.96	1.1757	63	65	0.51	0.078	IS1
Methyl tert-Butyl Ether	1634-04-4	88.15	0.7402	73	57	0.54	0.063	IS1
Vinyl Acetate	108-05-4	86.09	0.9317	86	43	5.3	1.2	IS1
2-Butanone (MEK)	78-93-3	72.11	0.7999	72	43	5.3	0.11	IS1
cis-1,2-Dichloroethene	156-59-2	96.94	1.2837	61	96	0.53	0.075	IS1
Diisopropyl Ether	108-20-3	102.18	0.7241	87	45,59,43	0.53	0.070	IS1
Ethyl Acetate	141-78-6	88.106	0.9003	61	70	1.1	0.28	IS1
n-Hexane	110-54-3	86.18	0.6548	57	86	0.53	0.11	IS1
Chloroform	67-66-3	119.4	1.4832	83	85	0.53	0.071	IS1
1,2-Dichloroethane-d4(S)	17060-07-0	-	-	65	67	-	-	IS1
Tetrahydrofuran	109-99-9	72.11	0.8892	72	71,42	0.53	0.067	IS1
Ethyl tert-Butyl Ether	637-92-3	102.176	0.7519	87	59,57	0.53	0.064	IS1
1,2-Dichloroethane	107-06-2	98.96	1.2351	62	64	0.53	0.059	IS1
1,4-Difluorobenzene(IS2)	540-36-3	-	-	114	88	-	-	-
1,1,1-Trichloroethane	71-55-6	133.4	1.3390	97	99, 61	0.54	0.066	IS2
Isopropyl acetate	108-21-4	102.13	0.8718	61	87,43	1.1	0.17	IS2
1-Butanol	71-36-3	74.1224	0.8098	56	41	1.1	0.14	IS2
Benzene	71-43-2	78.11	0.8765	78	77	0.53	0.077	IS2
Carbon Tetrachloride	56-23-5	153.8	1.5940	117	119	0.53	0.074	IS2

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	**CAS Number**	**Molecular Weight**	**Density**	**Primary Ion[2]**	**Secondary Ion(s)[2]**	**MRL[3] (µg/m³)**	**MDL[3] (µg/m³)**	**IS[4]**
Cyclohexane	110-82-7	84.16	0.7739	84	69,56	1.1	0.15	IS2
tert-Amyl Methyl Ether	994-05-8	102.176	0.7703	73	87,55,43	0.53	0.065	IS2
1,2-Dichloropropane	78-87-5	113	1.1560	63	62	0.53	0.066	IS2
Bromodichloromethane	75-27-4	163.8	1.980	83	85	0.53	0.077	IS2
Trichloroethene	79-01-6	131.4	1.4642	130	132	0.53	0.072	IS2
1,4-Dioxane	123-91-1	88.11	1.0337	88	58	0.53	0.063	IS2
Isooctane	540-84-1	114.23	0.6877	57	41	0.53	0.080	IS2
Methyl Methacrylate	80-62-6	100.12	0.944	100	69	1.1	0.19	IS2
n-Heptane	142-82-5	100.2	0.6837	71	57,100	0.53	0.085	IS2
cis-1,3-Dichloropropene	10061-01-5	111	1.224	75	77	0.56	0.083	IS2
4-Methyl-2-Pentanone	108-10-1	100.2	0.7965	58	85	0.53	0.073	IS2
trans-1,3-Dichloropropene	10061-02-6	111	1.217	75	77	0.53	0.11	IS2
1,1,2-Trichloroethane	79-00-5	133.4	1.4397	97	83	0.53	0.054	IS2
Chlorobenzene-d5(IS3)	3114-55-4	-	-	82	117	-	-	-
Toluene-d8(S)	2037-26-5	-	-	98	100	-	-	IS3
Toluene	108-88-3	92.14	0.8669	91	92	0.53	0.065	IS3
2-Hexanone	591-78-6	100.16	0.8113	43	58	0.53	0.066	IS3
Dibromochloromethane	124-48-1	208.3	2.451	129	127	0.53	0.070	IS3
1,2-Dibromoethane	106-93-4	187.9	2.1791	107	109	0.53	0.062	IS3
n-Butyl Acetate	123-86-4	116.16	0.8825	43	56, 73	0.53	0.073	IS3
n-Octane	111-65-9	114.23	0.6986	57	114	0.53	0.12	IS3

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	**CAS Number**	**Molecular Weight**	**Density**	**Primary Ion[2]**	**Secondary Ion(s)[2]**	**MRL[3] (µg/m³)**	**MDL[3] (µg/m³)**	**IS[4]**
Tetrachloroethene	127-18-4	165.8	1.6227	166	164	0.53	0.069	IS3
Chlorobenzene	108-90-7	112.6	1.1058	112	114	0.53	0.071	IS3
Ethylbenzene	100-41-4	106.2	0.8670	91	106	0.53	0.075	IS3
m-, p-Xylenes	179601-23-1	106.2	0.8642, 0.8611	91	106	1.1	0.14	IS3
Bromoform	75-25-2	252.8	2.899	173	175	0.53	0.11	IS3
Styrene	100-42-5	104.1	0.9060	104	78, 103	0.53	0.086	IS3
o-Xylene	95-47-6	106.2	0.8802	91	106	0.53	0.077	IS3
n-Nonane	111-84-2	128.26	0.7176	43	57, 85	0.53	0.089	IS3
1,1,2,2-Tetrachloroethane	79-34-5	167.9	1.5953	83	85	0.53	0.074	IS3
4-Bromofluorobenzene(S)	460-00-4	-	-	174	176	-	-	IS3
Cumene	98-82-8	120.2	0.8618	105	120	0.53	0.077	IS3
alpha-Pinene	80-56-8	136.24	0.8582	93	77	0.52	0.082	IS3
n-Propylbenzene	103-65-1	120.1938	0.8670	91	120,65	0.53	0.077	IS3
3-Ethyltoluene	620-14-4	120.2	0.8645	105	120	0.53	0.072	IS3
4-Ethyltoluene	622-96-8	120.2	0.8614	105	120	0.52	0.085	IS3
1,3,5-Trimethylbenzene	108-67-8	120.2	0.8652	105	120	0.52	0.077	IS3
alpha-Methylstyrene	98-83-9	118.19	0.9106	118	103,117	0.52	0.085	IS3
2-Ethyltoluene	611-14-3	120.2	0.8807	105	120	0.53	0.068	IS3
1,2,4-Trimethylbenzene	95-63-6	120.2	0.8758	105	120	0.53	0.074	IS3
n-Decane	124-18-5	142.28	0.7300	57	71,85	0.53	0.072	IS3
Benzyl Chloride	100-44-7	126.59	1.1004	91	126	1.1	0.12	IS3

TABLE 2 (Continued) - VOLATILE ORGANIC COMPOUNDS, EPA COMPENDIUM METHOD TO-15 (SCAN)								
Compound[1]	CAS Number	Molecular Weight	Density	Primary Ion[2]	Secondary Ion(s)[2]	MRL[3] (µg/m³)	MDL[3] (µg/m³)	IS[4]
1,3-Dichlorobenzene	541-73-1	147	1.2884	146	148	0.54	0.080	IS3
1,4-Dichlorobenzene	106-46-7	147	1.2475	146	148	0.53	0.082	IS3
sec-Butylbenzene	135-98-8	134.2206	0.8601	105	134,91	0.53	0.073	IS3
p-Isopropyltoluene	99-87-6	134.2206	0.8573	119	134,91	0.51	0.081	IS3
1,2,3-Trimethylbenzene	526-73-8	120.1938	0.8944	105	120	0.51	0.073	IS3
1,2-Dichlorobenzene	95-50-1	147	1.3059	146	148	0.54	0.079	IS3
d-Limonene	5989-27-5	136.24	0.8402	68	93	0.50	0.11	IS3
1,2,Dibromo-3-Chloropropane	96-12-8	236.33	2.093	157	75, 39	0.53	0.10	IS3
n-Undecane	1120-21-4	156.31	0.7402	57	71, 85	0.53	0.14	IS3
1,2,4-Trichlorobenzene	120-82-1	181.5	1.459	180	182, 184	0.55	0.13	IS3
Naphthalene	91-20-3	128.17	1.0253	128	129	0.53	0.13	IS3
n-Dodecane	112-40-3	170.34	0.7487	57	71,85	0.53	0.15	IS3
Hexachlorobutadiene	87-68-3	260.8	1.556	225	227	0.53	0.11	IS3
Cyclohexanone	108-94-1	98.14	0.9478	55	42, 98	0.52	0.083	IS3
tert-Butylbenzene	98-06-6	134.22	0.867	119	134	0.53	0.080	IS3
n-Butylbenzene	104-51-8	134.22	0.867	91	134	0.53	0.077	IS3

(S) = Surrogate (IS1) = Internal Standard 1 (IS2) = Internal Standard 2 (IS3) = Internal Standard 3
NA = Not Available

Note 1: Additional compounds may be reported as long as the minimum requirements of this document are met. The compounds listed in this table are reported using TO-15 SCAN. The Selected Ion Monitoring (SIM) compounds are a subset of this list and are included in Table 2A.

Note 2: These are suggested primary and secondary ions. However, any ions in the analyte spectra that are sufficient enough in response to reach the desired reporting limit and having a limited amount of interference, is acceptable for both the primary and secondary ion selection. Analyst experience should be utilized in determining appropriate ions.

Note 3: The laboratory performs three concentration level analyses (SIM, SCAN and Low Level SCAN). The method reporting limit listed is the standard SCAN limit (at or above lowest concentration in the initial calibration curve), but may change with each new initial calibration performed. Therefore, current reporting limits for the three analysis levels, MRLs in ppbv, and those from the Low Level SCAN should be reviewed in the electronic TO-15 Method Manual.

Note 4: The listing of the internal standard by which the compounds are quantitated is for TO-15 SCAN only. SIM compounds (SCAN subset) and their corresponding ions and internal standards are listed in Table 2A.

Note 5: m/e 101 is ~10% or less of m/e 85 (the base peak) and may not be present for low level results. Retention times must be carefully verified.

Table 2A – Volatile Organic Compounds, EPA Compendium Method TO-15 (SIM)					
Compound	**Primary Ion[1]**	**Secondary Ion[1]**	**MRL[2] (ug/m3)**	**MDL[2] (ug/m3)**	**IS**
Dichlorodifluoromethane	85	87	0.050	0.017	IS1
Chloromethane	52	50	0.050	0.019	IS1
Vinyl Chloride	62	64	0.025	0.0076	IS1
1,3-Butadiene	54	39	0.050	0.014	IS1
Bromomethane	94	96	0.025	0.0093	IS1
Chloroethane	64	66	0.025	0.0085	IS1
Acrolein	56	55	0.20	0.039	IS1
Acetone	58	43	2.5	0.056	IS1
Freon 11	101	103	0.050	0.015	IS1
1,1-Dichloroethene	96	98,61	0.025	0.0086	IS1
Methylene Chloride	84	49	0.10	0.013	IS1
Trichlorotrifluoroethane	151	153	0.025	0.0089	IS1
trans-1,2-Dichloroethene	96	98,61	0.025	0.0073	IS1
1,1-Dichloroethane	63	65	0.025	0.0061	IS1
Methyl tert-Butyl Ether	73	57	0.025	0.0093	IS1
cis-1,2-Dichloroethene	96	98,61	0.025	0.0092	IS1
Chloroform	83	85	0.10	0.018	IS1
1,2-Dichloroethane	62	64	0.025	0.0084	IS1
1,1,1-Trichloroethane	97	99	0.025	0.0059	IS1
Benzene	78	77	0.075	0.020	IS1
Carbon Tetrachloride	117	119	0.025	0.012	IS1
1,2-Dichloropropane	63	62,76	0.025	0.0073	IS2
Bromodichloromethane	83	85	0.025	0.0069	IS2
Trichloroethene	130	132	0.025	0.0085	IS2
1,4-Dioxane	88	58	0.10	0.0085	IS2
cis-1,3-Dichloropropene	75	77,39	0.025	0.0062	IS2
trans-1,3-Dichloropropene	75	77,39	0.025	0.0055	IS2
1,1,2-Trichloroethane	83	97,61	0.10	0.0079	IS2
Toluene	91	92	0.10	0.011	IS2
Dibromochloromethane	129	127	0.025	0.0088	IS3
1,2-Dibromoethane	107	109	0.025	0.0079	IS2
Tetrachloroethene	166	164	0.025	0.0082	IS2
Chlorobenzene	112	114	0.10	0.0092	IS3
Ethylbenzene	91	106	0.10	0.0097	IS3
m-&-p-Xylene	91	106	0.10	0.019	IS3
Styrene	104	103	0.10	0.0074	IS3
o-Xylene	91	106	0.10	0.0089	IS3
1,1,2,2-Tetrachloroethane	83	85	0.025	0.0072	IS3
1,3,5-Trimethylbenzene	105	120	0.10	0.0073	IS3
1,2,4-Trimethylbenzene	105	120	0.10	0.0083	IS3
1,3-Dichlorobenzene	146	148	0.025	0.0085	IS3
1,4-Dichlorobenzene	146	148	0.025	0.0081	IS3
1,2-Dichlorobenzene	146	148	0.025	0.0083	IS3
1,2-Dibromo-3-chloropropane	157	75	0.10	0.0095	IS3
1,2,4-Trichlorobenzene	182	184	0.050	0.013	IS3
Naphthalene	128	129	0.10	0.016	IS3
Hexachlorobutadiene	225	227	0.10	0.0092	IS3
Bromobenzene	77	156, 158	0.10	0.0042	IS3

NA = Not Available (IS1) = Internal Standard 1 (IS2) = Internal Standard 2 (IS3) = Internal Standard 3

Note 1: These are suggested primary and secondary ions. However, any ions in the analyte spectra that is sufficient enough in response to reach the desired reporting limit and having a limited amount of interference, is acceptable

for both the primary and secondary ion selection. Analyst experience should be utilized in determining appropriate ions.

Note 2: The method reporting limit listed is the standard SIM limit (lowest concentration in the initial calibration curve; must be higher than MDL), but may change with each new initial calibration performed. Therefore, current reporting limits should be reviewed. MDLs in ppbV may be reviewed in the electronic TO-15 Method Manual.

Table 3
Standard Concentrations (SCAN) (Primary Sources)[1]

Compound Name	0.1ng	0.2ng	0.5ng	1.0ng	5.0ng	25ng	50ng	100ng
Bromochloromethane (IS1)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Propene	0.1037	0.2074	0.5185	1.037	5.185	25.925	51.85	103.7
Dichlorodifluoromethane (CFC 12)	0.1048	0.2096	0.5240	1.048	5.240	26.200	52.40	104.8
Chloromethane	0.1006	0.2012	0.5030	1.006	5.030	25.150	50.30	100.6
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	0.1021	0.2042	0.5105	1.021	5.105	25.525	51.05	102.1
Vinyl Chloride	0.1032	0.2064	0.5160	1.032	5.160	25.800	51.60	103.2
1,3-Butadiene	0.1059	0.2118	0.5295	1.059	5.295	26.475	52.95	105.9
Bromomethane	0.0993	0.1986	0.4965	0.993	4.965	24.825	49.65	99.3
Chloroethane	0.1012	0.2024	0.5060	1.012	5.060	25.300	50.60	101.2
Ethanol	0.5271	1.0542	2.6355	5.271	26.355	131.775	263.55	527.1
Acetonitrile	0.1059	0.2118	0.5295	1.059	5.295	26.475	52.95	105.9
Acrolein	0.1054	0.2108	0.5270	1.054	5.270	26.350	52.70	105.4
Acetone	0.5322	1.0644	2.6610	5.322	26.610	133.050	266.10	532.2
Trichlorofluoromethane	0.1051	0.2102	0.5255	1.051	5.255	26.275	52.55	105.1
Isopropyl Alcohol	0.2107	0.4214	1.0535	2.107	10.535	52.675	105.35	210.7
Acrylonitrile	0.1056	0.2112	0.5280	1.056	5.280	26.400	52.80	105.6
1,1-Dichloroethene	0.1061	0.2122	0.5305	1.061	5.305	26.525	53.05	106.1
tert-Butanol	0.2120	0.4240	1.0600	2.120	10.600	53.000	106.00	212.0
Methylene Chloride	0.1058	0.2116	0.5290	1.058	5.290	26.450	52.90	105.8
Allyl Chloride	0.1054	0.2108	0.5270	1.054	5.270	26.350	52.70	105.4
Trichlorotrifluoroethane	0.1053	0.2106	0.5265	1.053	5.265	26.325	52.65	105.3
Carbon Disulfide	0.1063	0.2126	0.5315	1.063	5.315	26.575	53.15	106.3
trans-1,2-Dichloroethene	0.1081	0.2162	0.5405	1.081	5.405	27.025	54.05	108.1
1,1-Dichloroethane	0.1022	0.2044	0.5110	1.022	5.110	25.550	51.10	102.2
Methyl tert-Butyl Ether	0.1070	0.2140	0.5350	1.070	5.350	26.750	53.50	107.0
Vinyl Acetate	0.5281	1.0562	2.6405	5.281	26.405	132.025	264.05	528.1
2-Butanone (MEK)	0.1052	0.2104	0.5260	1.052	5.260	26.300	52.60	105.2
cis-1,2-Dichloroethene	0.1067	0.2134	0.5335	1.067	5.335	26.675	53.35	106.7
Diispropyl Ether	0.1065	0.2130	0.5325	1.065	5.325	26.625	53.25	106.5
Ethyl Acetate	0.2136	0.4272	1.0680	2.136	10.680	53.400	106.80	213.6
n-Hexane	0.1066	0.2132	0.5330	1.066	5.330	26.650	53.30	106.6
Chloroform	0.1061	0.2122	0.5305	1.061	5.305	26.525	53.05	106.1
1,2-Dichloroethane-d4 (S)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Tetrahydrofuran	0.1064	0.2128	0.5320	1.064	5.320	26.600	53.20	106.4
Ethyl tert-Butyl Ether	0.1059	0.2118	0.5295	1.059	5.295	26.475	52.95	105.9
1,2-Dichloroethane	0.1055	0.2110	0.5275	1.055	5.275	26.375	52.75	105.5
1,4-Difluorobenzene(IS2)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
1,1,1-Trichloroethane	0.1077	0.2154	0.5385	1.077	5.385	26.925	53.85	107.7
Isopropyl acetate	0.2113	0.4226	1.0565	2.113	10.565	52.825	105.65	211.3
1-Butanol	0.2114	0.4228	1.0570	2.114	10.570	52.850	105.70	211.4

Table 3 - Continued
Standard Concentrations (SCAN) (Primary Sources)[1]

Compound Name	0.1ng	0.2ng	0.5ng	1.0ng	5.0ng	25ng	50ng	100ng
Benzene	0.1057	0.2114	0.5285	1.057	5.285	26.425	52.85	105.7
Carbon Tetrachloride	0.1060	0.2120	0.5300	1.060	5.300	26.500	53.00	106.0
Cyclohexane	0.2135	0.4270	1.0675	2.135	10.675	53.375	106.75	213.5
tert-Amyl Methyl Ether	0.1057	0.2114	0.5285	1.057	5.285	26.425	52.85	105.7
1,2-Dichloropropane	0.1066	0.2132	0.5330	1.066	5.330	26.650	53.30	106.6
Bromodichloromethane	0.1067	0.2134	0.5335	1.067	5.335	26.675	53.35	106.7
Trichloroethene	0.1061	0.2122	0.5305	1.061	5.305	26.525	53.05	106.1
1,4-Dioxane	0.1063	0.2126	0.5315	1.063	5.315	26.575	53.15	106.3
Isooctane	0.1060	0.2120	0.5300	1.060	5.300	26.500	53.00	106.0
Methyl Methacrylate	0.2112	0.4224	1.0560	2.112	10.560	52.800	105.60	211.2
n-Heptane	0.1065	0.2130	0.5325	1.065	5.325	26.625	53.25	106.5
cis-1,3-Dichloropropene	0.1120	0.2240	0.5600	1.120	5.600	28.000	56.00	112.0
4-Methyl-2-Pentanone	0.1059	0.2118	0.5295	1.059	5.295	26.475	52.95	105.9
trans-1,3-Dichloropropene	0.1067	0.2134	0.5335	1.067	5.335	26.675	53.35	106.7
1,1,2-Trichloroethane	0.1064	0.2128	0.5320	1.064	5.320	26.600	53.20	106.4
Chlorobenzene-d5 (IS3)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Toluene-d8 (S)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Toluene	0.1054	0.2108	0.5270	1.054	5.270	26.350	52.70	105.4
2-Hexanone	0.1060	0.2120	0.5300	1.060	5.300	26.500	53.00	106.0
Dibromochloromethane	0.1061	0.2122	0.5305	1.061	5.305	26.525	53.05	106.1
1,2-Dibromoethane	0.1064	0.2128	0.5320	1.064	5.320	26.600	53.20	106.4
n-Butyl Acetate	0.1068	0.2136	0.5340	1.068	5.340	26.700	53.40	106.8
n-Octane	0.1060	0.2120	0.5300	1.060	5.300	26.500	53.00	106.0
Tetrachloroethene	0.1063	0.2126	0.5315	1.063	5.315	26.575	53.15	106.3
Chlorobenzene	0.1066	0.2132	0.5330	1.066	5.330	26.650	53.30	106.6
Ethylbenzene	0.1052	0.2104	0.5260	1.052	5.260	26.300	52.60	105.2
m- & p-Xylene	0.2123	0.4246	1.0615	2.123	10.615	53.075	106.15	212.3
Bromoform	0.1063	0.2126	0.5315	1.063	5.315	26.575	53.15	106.3
Styrene	0.1058	0.2116	0.5290	1.058	5.290	26.450	52.90	105.8
o-Xylene	0.1055	0.2110	0.5275	1.055	5.275	26.375	52.75	105.5
n-Nonane	0.1054	0.2108	0.5270	1.054	5.270	26.350	52.70	105.4
1,1,2,2-Tetrachloroethane	0.1057	0.2114	0.5285	1.057	5.285	26.425	52.85	105.7
4-Bromofluorobenzene (S)	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**	**12.5**
Cumene	0.1052	0.2104	0.5260	1.052	5.260	26.300	52.60	105.2
alpha-Pinene	0.1046	0.2092	0.5230	1.046	5.230	26.150	52.30	104.6
n-Propylbenzene	0.1064	0.2128	0.5320	1.064	5.320	26.600	53.20	106.4
3-Ethyltoluene	0.1050	0.2100	0.5250	1.050	5.250	26.250	52.50	105.0
4-Ethyltoluene	0.1049	0.2098	0.5245	1.049	5.245	26.225	52.45	104.9
1,3,5-Trimethylbenzene	0.1049	0.2098	0.5245	1.049	5.245	26.225	52.45	104.9
alpha-Methylstyrene	0.1049	0.2098	0.5245	1.049	5.245	26.225	52.45	104.9
2-Ethyltoluene	0.1060	0.2120	0.5300	1.060	5.300	26.500	53.00	106.0
1,2,4-Trimethylbenzene	0.1051	0.2102	0.5255	1.051	5.255	26.275	52.55	105.1

Table 3 - Continued
Standard Concentrations (SCAN) (Primary Sources)[1]

Compound Name	0.1ng	0.2ng	0.5ng	1.0ng	5.0ng	25ng	50ng	100ng
n-Decane	0.1059	0.2118	0.5295	1.059	5.295	26.475	52.95	105.9
Benzyl Chloride	0.1074	0.2148	0.5370	1.074	5.370	26.850	53.70	107.4
1,3-Dichlorobenzene	0.1071	0.2142	0.5355	1.071	5.355	26.775	53.55	107.1
1,4-Dichlorobenzene	0.1064	0.2128	0.5320	1.064	5.320	26.600	53.20	106.4
sec-Butylbenzene	0.1055	0.2110	0.5275	1.055	5.275	26.375	52.75	105.5
p-Isopropyltoluene	0.1026	0.2052	0.5130	1.026	5.130	25.650	51.30	102.6
1,2,3-Trimethylbenzene	0.1026	0.2052	0.5130	1.026	5.130	25.650	51.30	102.6
1,2-Dichlorobenzene	0.1083	0.2166	0.5415	1.083	5.415	27.075	54.15	108.3
d-Limonene	0.1005	0.2010	0.5025	1.005	5.025	25.125	50.25	100.5
1,2-Dibromo-3-Chloropropane	0.1051	0.2102	0.5255	1.051	5.255	26.275	52.55	105.1
n-Undecane	0.1053	0.2106	0.5265	1.053	5.265	26.325	52.65	105.3
1,2,4-Trichlorobenzene	0.1097	0.2194	0.5485	1.097	5.485	27.425	54.85	109.7
Naphthalene	0.1056	0.2112	0.5280	1.056	5.280	26.400	52.80	105.6
n-Dodecane	0.1056	0.2112	0.5280	1.056	5.280	26.400	52.80	105.6
Hexachlorobutadiene	0.1057	0.2114	0.5285	1.057	5.285	26.425	52.85	105.7
Methacrylonitrile	0.1067	0.2134	0.5335	1.067	5.335	26.675	53.35	106.7
Cyclohexanone	0.1039	0.2078	0.5195	1.039	5.195	25.975	51.95	103.9
tert-Butylbenzene	0.1050	0.2100	0.5250	1.050	5.250	26.250	52.50	105.0
n-Butylbenzene	0.1054	0.2108	0.5270	1.054	5.270	26.350	52.70	105.4

Note 1: The concentrations detailed in this table may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Table 3A - Standard Concentrations (SIM) (Primary Sources)[1]

Compound Name	20pg	50pg	100pg	500pg	1000pg	2000pg	5000pg	10,000pg	25,000pg	50,000pg
Freon-12	20.96	52.40	104.8	524.0	1048	2096	5240	10480	26200	52400
Chloromethane	20.12	50.30	100.6	503.0	1006	2012	5030	10060	25150	50300
Vinyl Chloride	20.64	51.60	103.2	516.0	1032	2064	5160	10320	25800	51600
1,3-Butadiene	21.18	52.95	105.9	529.5	1059	2118	5295	10590	26475	52950
Bromomethane	19.86	49.65	99.3	496.5	993	1986	4965	9930	24825	49650
Chloroethane	20.24	50.60	101.2	506.0	1012	2024	5060	10120	25300	50600
Acrolein	21.08	52.70	105.4	527.0	1054	2108	5270	10540	26350	52700
Acetone	106.44	266.10	532.2	2661.0	5322	10644	26610	53220	133050	266100
Freon-11	21.02	52.55	105.1	525.5	1051	2102	5255	10510	26275	52550
1,1-Dichloroethene	21.22	53.05	106.1	530.5	1061	2122	5305	10610	26525	53050
Methylene Chloride	21.16	52.90	105.8	529.0	1058	2116	5290	10580	26450	52900
Freon-113	21.06	52.65	105.3	526.5	1053	2106	5265	10530	26325	52650
trans-1,2-Dichloroethene	21.62	54.05	108.1	540.5	1081	2162	5405	10810	27025	54050
1,1-Dichloroethane	20.44	51.10	102.2	511.0	1022	2044	5110	10220	25550	51100
Methyl tert-Butyl Ether	21.40	53.50	107.0	535.0	1070	2140	5350	10700	26750	53500
cis-1,2-Dichloroethene	21.34	53.35	106.7	533.5	1067	2134	5335	10670	26675	53350
Chloroform	21.22	53.05	106.1	530.5	1061	2122	5305	10610	26525	53050
1,2-Dichloroethane	21.10	52.75	105.5	527.5	1055	2110	5275	10550	26375	52750
1,1,1-Trichloroethane	21.54	53.85	107.7	538.5	1077	2154	5385	10770	26925	53850
Benzene	21.14	52.85	105.7	528.5	1057	2114	5285	10570	26425	52850
Carbon Tetrachloride	21.20	53.00	106.0	530.0	1060	2120	5300	10600	26500	53000
1,2-Dichloropropane	21.32	53.30	106.6	533.0	1066	2132	5330	10660	26650	53300
Bromodichloromethane	21.34	53.35	106.7	533.5	1067	2134	5335	10670	26675	53350
Trichloroethene	21.22	53.05	106.1	530.5	1061	2122	5305	10610	26525	53050
1,4-Dioxane	21.26	53.15	106.3	531.5	1063	2126	5315	10630	26575	53150
cis-1,3-Dichloropropene	22.40	56.00	112.0	560.0	1120	2240	5600	11200	28000	56000
trans-1,3-Dichloropropene	21.34	53.35	106.7	533.5	1067	2134	5335	10670	26675	53350
1,1,2-Trichloroethane	21.28	53.20	106.4	532.0	1064	2128	5320	10640	26600	53200
Toluene	21.08	52.70	105.4	527.0	1054	2108	5270	10540	26350	52700
Dibromochloromethane	21.22	53.05	106.1	530.5	1061	2122	5305	10610	26525	53050
1,2-Dibromoethane	21.28	53.20	106.4	532.0	1064	2128	5320	10640	26600	53200
Tetrachloroethene	21.26	53.15	106.3	531.5	1063	2126	5315	10630	26575	53150
Chlorobenzene	21.32	53.30	106.6	533.0	1066	2132	5330	10660	26650	53300
Ethylbenzene	21.04	52.60	105.2	526.0	1052	2104	5260	10520	26300	52600
m,p-Xylenes	42.46	106.15	212.3	1061.5	2123	4246	10615	21230	53075	106150
Styrene	21.16	52.90	105.8	529.0	1058	2116	5290	10580	26450	52900
o-Xylene	21.10	52.75	105.5	527.5	1055	2110	5275	10550	26375	52750
1,1,2,2-Tetrachloroethane	21.14	52.85	105.7	528.5	1057	2114	5285	10570	26425	52850
1,3,5-Trimethylbenzene	20.98	52.45	104.9	524.5	1049	2098	5245	10490	26225	52450
1,2,4-Trimethylbenzene	21.02	52.55	105.1	525.5	1051	2102	5255	10510	26275	52550
1,3-Dichlorobenzene	21.42	53.55	107.1	535.5	1071	2142	5355	10710	26775	53550
1,4-Dichlorobenzene	21.28	53.20	106.4	532.0	1064	2128	5320	10640	26600	53200
1,2-Dichlorobenzene	21.66	54.15	108.3	541.5	1083	2166	5415	10830	27075	54150
1,2-Dibromo-3-chloropropane	21.02	52.55	105.1	525.5	1051	2102	5255	10510	26275	52550
1,2,4-Trichlorobenzene	21.94	54.85	109.7	548.5	1097	2194	5485	10970	27425	54850
Naphthalene	21.12	52.80	105.6	528.0	1056	2112	5280	10560	26400	52800
Hexachloro-1,3-butadiene	21.14	52.85	105.7	528.5	1057	2114	5285	10570	26425	52850

Table 3A - Standard Concentrations (SIM) (Primary Sources)[1] – Continued

Compound Name	20pg	50pg	100pg	500pg	1000pg	2000pg	5000pg	10,000pg
Bromobenzene	21.2	53.0	106	530	1060	2120	5300	10600

Note 1: The concentrations detailed in Table 3A may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Table 4 - Standard Concentrations (SCAN) (Secondary Sources)[1]

Compound Name	25ng	Compound Name	25ng	Compound Name	25ng
Bromochloromethane (IS1)	**12.5**	1,1,1-Trichloroethane	26.525	alpha-Pinene	26.600
Propene	26.275	Isopropyl acetate	53.275	n-Propylbenzene	26.750
Dichlorodifluoromethane (CFC 12)	26.600	1-Butanol	53.300	3-Ethyltoluene	26.450
Chloromethane	26.250	Benzene	26.625	4-Ethyltoluene	26.425
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)	26.325	Carbon Tetrachloride	26.700	1,3,5-Trimethylbenzene	26.500
Vinyl Chloride	26.350	Cyclohexane	53.150	alpha-Methylstyrene	26.525
1,3-Butadiene	26.225	tert-Amyl Methyl Ether	26.550	2-Ethyltoluene	26.700
Bromomethane	26.225	1,2-Dichloropropane	26.525	1,2,4-Trimethylbenzene	26.550
Chloroethane	26.250	Bromodichloromethane	26.700	n-Decane	26.625
Ethanol	130.375	Trichloroethene	26.550	Benzyl Chloride	26.550
Acetonitrile	26.200	1,4-Dioxane	26.600	1,3-Dichlorobenzene	26.475
Acrolein	26.075	Isooctane	26.525	1,4-Dichlorobenzene	26.750
Acetone	131.825	Methyl Methacrylate	52.950	sec-Butylbenzene	26.575
Trichlorofluoromethane	26.025	n-Heptane	26.625	p-Isopropyltoluene	26.600
Isopropyl Alcohol	52.775	cis-1,3-Dichloropropene	26.025	1,2,3-Trimethylbenzene	26.600
Acrylonitrile	26.450	4-Methyl-2-Pentanone	26.650	1,2-Dichlorobenzene	26.750
1,1-Dichloroethene	26.675	trans-1,3-Dichloropropene	26.625	d-Limonene	26.625
tert-Butanol	53.350	1,1,2-Trichloroethane	26.500	1,2-Dibromo-3-Chloropropane	26.300
Methylene Chloride	26.600	**Chlorobenzene-d5 (IS3)**	**12.5**	n-Undecane	26.775
Allyl Chloride	26.525	**Toluene-d8 (S)**	**12.5**	1,2,4-Trichlorobenzene	27.200
Trichlorotrifluoroethane	26.750	Toluene	26.400	Naphthalene	26.125
Carbon Disulfide	26.725	2-Hexanone	26.425	n-Dodecane	26.825
trans-1,2-Dichloroethene	26.700	Dibromochloromethane	26.450	Hexachlorobutadiene	26.550
1,1-Dichloroethane	26.525	1,2-Dibromoethane	26.425	Methacrylonitrile	26.500
Methyl tert-Butyl Ether	26.625	Butyl Acetate	26.850	Cyclohexanone	26.150
Vinyl Acetate	132.750	n-Octane	26.525	tert-Butylbenzene	26.525
2-Butanone (MEK)	26.450	Tetrachloroethene	26.500	n-Butylbenzene	26.575
cis-1,2-Dichloroethene	26.475	Chlorobenzene	26.525		
Diisopropyl Ether	26.600	Ethylbenzene	26.475		
Ethyl Acetate	53.300	m- & p-Xylene	52.975		
n-Hexane	26.625	Bromoform	26.525		
Chloroform	26.500	Styrene	26.350		
1,2-Dichloroethane-d4 (S)	**12.5**	o-Xylene	26.400		
Tetrahydrofuran	26.550	n-Nonane	26.500		
Ethyl tert-Butyl Ether	26.525	1,1,2,2-Tetrachloroethane	26.450		
1,2-Dichloroethane	26.500	**4-Bromofluorobenzene (S)**	**12.5**		
1,4-Difluorobenzene(IS2)	**12.5**	Cumene	26.525		

Note 1: The concentrations detailed in this table may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Table 4A – ICV/LCS Standard Concentrations (SIM) (Secondary Sources)[1]

Compound Name	500pg
Freon-12	532.0
Chloromethane	525.0
Vinyl Chloride	527.0
1,3-Butadiene	524.5
Bromomethane	524.5
Chloroethane	525.0
Acrolein	521.5
Acetone	2636.5
Freon-11	520.5
1,1-Dichloroethene	533.5
Methylene Chloride	532.0
Freon-113	535.0
trans-1,2-Dichloroethene	534.0
1,1-Dichloroethane	530.5
Methyl tert-Butyl Ether	532.5
cis-1,2-Dichloroethene	529.5
Chloroform	530.0
1,2-Dichloroethane	530.0
1,1,1-Trichloroethane	530.5
Benzene	532.5
Carbon Tetrachloride	534.0
1,2-Dichloropropane	530.5
Bromodichloromethane	534.0
Trichloroethene	531.0
1,4-Dioxane	532.0
cis-1,3-Dichloropropene	520.5
trans-1,3-Dichloropropene	532.5
1,1,2-Trichloroethane	530.0
Toluene	528.0
Dibromochloromethane	529.0
1,2-Dibromoethane	528.5
Tetrachloroethene	530.0
Chlorobenzene	530.5
Ethylbenzene	529.5
m,p-Xylenes	1059.5
Styrene	527.0
o-Xylene	528.0
1,1,2,2-Tetrachloroethane	529.0
1,3,5-Trimethylbenzene	530.0
1,2,4-Trimethylbenzene	531.0
1,3-Dichlorobenzene	529.5
1,4-Dichlorobenzene	535.0
1,2-Dichlorobenzene	535.0
1,2-Dibromo-3-chloropropane	526.0
1,2,4-Trichlorobenzene	544.0
Naphthalene	522.5
Hexachloro-1,3-butadiene	531.0
Bromobenzene	1060

Note 1: The concentrations detailed in this table may change with each standard purchased or internally prepared. Refer to the appropriate initial calibration file, where necessary for the corresponding concentrations.

Attachment 1

Training Plan

Training Plan for Analysis of VOCs by GC/MS

Trainee _____ Trainer _____ Instrument _____ Training Completion Date _____

1. Read SOP *Training Duration* _____ Trainer ___ Trainee ___ Date _____

2. Read Methods TO-14A & TO-15A *Training Duration* _____ Trainer ___ Trainee ___ Date _____

3. Demonstrated understanding of the scientific basis of the analysis Trainer ___ Trainee ___ Date _____
   Whole air sample preconcentration techniques
   Gas chromatography *Training Duration* _____
   Mass spectrometry

4. Demonstrated familiarity with related SOPs Trainer ___ Trainee ___ Date _____
   SOP for Batches and Sequences; Rev. ___
   SOP for Making Entries onto Analytical Records; Rev. ___ *Training Duration* _____
   SOP for Manual Integration Policy; Rev. ____
   SOP for Significant Figures; Rev. ____
   SOP for Nonconformance and Corrective Action; Rev. ____
   SOP for Performing MDL Studies and Establishing Limits of Detection and Quantitation; Rev. ____
   SOP for Cleaning and Certification of Summa Canisters; Rev. ____

5. Observe performance of SOP *Training Duration* _____ Trainer ___ Trainee ___ Date _____
   ___sample preparation/dilution and sample loading and analysis
   ___analytical sequence setup
   ___standard preparation
   ___BFB tuning evaluation
   ___initial calibration (model, calculations, manual integrations)/initial calibration verification
   ___manual integrations
   ___continuing calibration verification
   ___EnviroQuant introduction (recognizing saturation and sensitivity issues)
   ___data reduction and reporting including reporting req. for various agencies, autotexts, documentation
   ___canister and bag handling (including leakers)

6. Perform SOP with supervision *Training Duration* _____ Trainer ___ Trainee ___ Date _____
   ___sample preparation/dilution and sample loading and analysis
   ___analytical sequence setup
   ___standard preparation
   ___BFB tuning evaluation
   ___initial calibration (model, calculations, manual integrations)/initial calibration verification
   ___manual integrations
   ___continuing calibration verification
   ___EnviroQuant use (recognizing saturation and sensitivity issues)
   ___data reduction and reporting including reporting req. for various agencies, autotexts, documentation
   ___canister and bag handling (including leakers)

7. Independent performance of the SOP *Training Duration* _____ Trainer ___ Trainee ___ Date _____
   ___sample preparation/dilution and sample loading and analysis
   ___analytical sequence setup
   ___standard preparation
   ___BFB tuning evaluation
   ___initial calibration (model, calculations, manual integrations)/initial calibration verification
   ___manual integrations
   ___continuing calibration verification
   ___EnviroQuant proficiency (recognizing saturation and sensitivity issues)
   ___data reduction and reporting including reporting req. for various agencies, autotexts, documentation
   ___canister and bag handling (including leakers)
   ___initial demonstration of competency (4 Laboratory Control Samples)

8. Instrument operation and maintenance Trainer ___ Trainee ___ Date _____
   ___autosampler *Training Duration* _____
   ___GC and capillary column installation *Training Duration* _____
   ___mass spectrometer *Training Duration* _____
   ___data system *Training Duration* _____

Attachment 2

Initial Calibration Checklist

Initial Calibration Review Checklist - EPA Compendium Method TO-15

ICAL Date:_____ ICAL ID:_____ LIMS ICAL ID:_____

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan Scan Low Level (0.1ng): ☐ Yes ☐ No

Analyst		Reviewer
☐	1. Is the required documentation in the ICAL file?	☐
	☐ BFB Tune analysis Report	☐
	☐ Calibration Status Report (aka Calibration History)	☐
	☐ Response Factor Report/Percent RSD	☐
	☐ Quant Report for each calibration std (including manual integration documentation)	☐
	☐ ICV Quantitation Report	☐
	☐ TO-15 Standard Calculation Spreadsheet	☐
☐	2. Was the ICAL performed continuously (not interrupted for maintenance or sample analysis)?	☐
☐	3. Have all the calibration standards been analyzed within 24 hours of each other?	☐
☐	4. Does the BFB tune check standard analysis at the start meet the tune criteria?	☐
☐	5. Are all the analytes in the blank analysis <MRL?	☐
☐	6. Does each analyte's ICAL include a minimum of 5 concentrations at 5 consecutive levels?	☐
☐	7. Were the standards analyzed from low concentration to high concentration?	☐
☐	8. For each analyte, are there no levels skipped?	☐
☐	9. For each analyte, is there only one value used for each calibration level?	☐
☐	10. For each analyte, is the lowest standard's concentration at or below the analyte's MRL?	☐
☐	11. For each analyte, is the corresponding signal to noise ratio at least 3:1 at the lowest point on the curve?	☐
☐	12. For each analyte, are the corresponding upper levels free from saturation?	☐
☐	13. If a calibration level is dropped, are all the responses for each target analyte dropped and is the information noted in the ICAL explaining the reason?	☐
☐	14. Is the average RSD ≤30% for all analytes, with no more than two exceptions ≤40%?	☐
☐	15. DoD/Navy: Is the average RSD ≤30% for all analytes?	☐
☐	16. Is the response Y at each calibration level within 40% of the mean area response over the initial calibration range for each internal standard?	☐
☐	17. Percent recovery for each analyte in the ICV 70%-130% (AZ: 50-150% for VA)?	☐
☐	18. Was the RRT for each target compound at each calibration level within 0.06RRT units of the mean RRT for the compound?	☐
☐	19. Is the retention time shift for each of the internal standards at each calibration level within 20s of the mean retention time over the initial calibration range for each standard?	☐
☐	20. If there are any manual integrations, are they performed correctly according to the corresponding SOP? If so, initial and date the appropriate pages.	☐
☐	21. Is the ICAL good at 0.5ng (or 0.1ng)–100ng (Scan) or 10-20000pg (SIM) for all compounds? ☐ Yes ☐ No Note exceptions and corresponding MRLs below – *Specify applicable range...*	☐
☐	22. Are ALL of the peak selections for each analyte correct according to retention time (all RTs must be checked by both the initial and peer reviewer)?	☐

COMMENTS:

Analyst: _____ Secondary Reviewer: _____

Attachment 3

Daily QC and Sample Review Checklists

EPA Compendium Method TO-15 - Daily QC Review Checklist

(Note exceptions in Comments and include Analysis Observations/Case Narrative Summary Form as appropriate)

Method: ☐ EPA TO-15 ☐ EPA TO-14A **Analysis Date:** _____

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan **Scan Low Level (0.1ng):** ☐ Yes ☐ No **DOD:** ☐ Yes ☐ No

Analyst **Reviewer**

☐ 1. Is the required documentation present? ..... ☐
- ☐ CORRECT BFB Tune analysis Report
- ☐ CCV analysis Quantitation Report & %D Report
- ☐ LCS analysis Quantitation Report
- ☐ MB analysis Quantitation Report

☐ 2. BFB **tune** check standard analysis meet the tune criteria for the method indicated above? ..... ☐

☐ 3. Analyses within the tune's **24-hr window or** ☐ **Client's 12hr window requirement**? ..... ☐

☐ 4. Does the **CCV** have a difference ≤30% for all analytes? ..... ☐
[Note all outliers biased high and/or low]

☐ 5. **DoD**: Does the **Closing CCV** have a difference ≤30% for all analytes? ..... ☐
[Note all outliers biased high and/or low]

☐ 6. All **IS** retention times within 20 seconds of the CCV RT or the RT from the midpoint (ICAL)? ..... ☐

☐ 7. All **IS** responses within ±40% of CCV or the midpoint in the ICAL? ..... ☐

☐ 8. All **surrogate** recoveries (in CCVs, MB, LCSs, etc.) within acceptance limits (70%-130%) ..... ☐

☐ 9. All analytes in the **MB** <MRL? (DoD <1/2MRL, except Acetone, MeCl2, EtOH, Carbon Disulfide)? ..... ☐

☐ 10. **LCS** %R within lab control limits for all analytes except AZ samples (70%-130%, VA 50%-150%)? ..... ☐

☐ 11. All analytes in the **Lab Duplicate / DLCS** within ±25% or the client specified limits? ..... ☐

☐ 12. **DoD/Navy**: **DLCS** analyzed? ..... ☐

Air-Phase Petroleum Hydrocarbons

☐ 1. Does the **CCV** meet the following criteria? ..... ☐
- Percent difference ≤30%.
- One compound or range can be >30%, but less than 50%.
- No single analyte or range may be >50%.

[Note outliers biased high and/or low in comments below]

☐ 2. Does lab **duplicate** meet an RPD of ≤30% for results >5x MRL? Repeat analysis if: ..... ☐

RPD >30 (where both analyses are >5x RL	1st analysis detect @ >5x MRL, Dup=ND
1st analysis ≤5x RL; Dup=ND (RPD not calculable)	

☐ 3. Are the analytes in the **LCS** within 70%-130% recovery? ..... ☐

COMMENTS:

Analyst/LIMS Run Approval: _____ Secondary/LIMS Supervisor Approval: _____

EPA Compendium Method TO-15 - Sample Review Checklist

(Note exceptions in Comments and include Analysis Observations/Case Narrative Summary Form as appropriate)

Method: ☐ EPA TO-15 ☐ EPA TO-14A **Analysis Date:** _____ **Project #:** _____

Instrument: ☐ MS8 ☐ MS9 ☐ MS13 ☐ MS16 ☐ MS19 ☐ MS21 ☐ MS22

Mode: ☐ SIM ☐ Scan **Scan Low Level (0.1ng):** ☐ Yes ☐ No **DOD:** ☐ Yes ☐ No

Analyst		Reviewer
☐	1. All analyte hits in the samples within the **calibration range** and/or noted?	☐
☐	2. All **peak integrations** acceptable?	☐
☐	3. All **manual integrations** flagged and documented?	☐
☐	4. Have **Q values** been verified for each peak?	☐
☐	5. All **calculations** correct?	☐
☐	6. Has the analyst initialed and dated each **quantitation report**?	☐
☐	7. For **TICs** are the relative intensity and other requirements met (associated MB reported)?	☐
☐	8. **Auto report** correct?	☐
☐	9. **MRL** = _____ ☐ ng ☐ pg (ethanol, acetone, vinyl acetate = 5.0ng)	☐
☐	10. Pressurized with **Helium**? Is the worksheet completed for all samples?	☐
☐	11. Report to **MDL**? ☐ Yes ☐ No	☐
☐	12. **Global Minimum Detection Limit** = _____ ☐ ng ☐ pg	☐
☐	13. **DOD:** Are **manual integrations** notated in the **case narrative?**	☐

Air-Phase Petroleum Hydrocarbons

☐	1. Are all manual **integrations** flagged and documented (except for HC ranges)?	☐
☐	2. Are the associated ICAL responses correct?	☐
☐	3. Does the lab **duplicate** meet RPD ≤30% for results >5x the MRL? Otherwise, repeat analyses if:	☐

RPD >30 (where both analyses are >5x RL	1st analysis detect @ >5x MRL, Dup=ND
1st analysis ≤5x RL; Dup=ND (RPD not calculable)	

COMMENTS:

☐	1. **CASE NARRATIVE COMPLETED?**	☐

Analyst/LIMS Run Approval: _____ Secondary/LIMS Supervisor Approval: _____

Attachment 4

State and Project Specific Requirements

Minnesota Requirements	
Item	**Criteria**
Holding Time (HT)	14 days
Tedlar bags	Not allowed for sampling or sample dilution
Canisters and flow controllers	Individually certified Individually leak checked before shipment
	Samples with concentrations outside of the calibration curve will have a zero canister analysis performed to check for carryover. If carryover is detected, system bake out shall be performed and documented. Additionally, in instances where the laboratory has evidence on file that a particular compound when present at a high concentration does not exhibit carry-over, the samples will not be reanalyzed. When samples are analyzed that have a higher concentration than the evidence on file, the above requirements must be followed. Also, samples that have hits below the MRL will not be reanalyzed when analyzed after a sample with concentrations over the calibration range.
Method Reporting Verification Check	Analyze a Method Reporting Verification at the beginning of the sequence prior to analyzing samples. Acceptance criteria ±40%.
Duplicates	10 percent laboratory duplicates
Record retention	MN/NELAP 5 years MPCA (Minnesota Pollution Control Agency) compliant samples 10 years
Tier level	TIII

Arizona Requirements	
Item	**Criteria**
LCS	70-130% (vinyl acetate 50-150%)

Department of Toxic Substances Control (DTSC) Requirements	
Item	**Criteria**
Holding Time (HT)	72 hour hold time for canisters

EPA Region 9 Requirements	
Item	**Criteria**
Holding Time (HT)	14 days

Attachment 5

Tekmar AutoCan Trap Packing Instructions

Tekmar AutoCan Trap Packing Instructions

The internal sample trap on the AutoCan is a 1/8" x 12" thin-walled stainless steel tube, usually coated with fused silica (Silcosteel). It is packed with a combination of graphitized carbon black and carbon molecular sieve adsorbents, with the weakest adsorbent at the top (inlet) and the strongest at the bottom (outlet). Each bed is separated by a small plug of untreated glass wool. Untreated is used because DCMS-treated wool will release siloxanes when heated to the temperatures used for TO-15 analysis.

The adsorbents listed below are further refined at the lab by sifting in an 80-mesh sieve. This removes the smaller particles and leaves a very uniform product of about 60-mesh size. Getting rid of the "fines" helps ensure good flow through the trap during sampling and reduces the pressure drop across the trap. A tightly-packed trap can lead to problems such as poor reproducibility, slowed flow rates, and channeling (small spaces in the beds that let analytes pass through).

Adsorbent	Mesh	Supplier	Catalog #	Packing Amount (mg)
Carbosieve SIII	60/80	Supelco	10184	40
Carbosieve G	60/80	Supelco	10198	30
Carbopack Z	60/80	Supelco	20273	30
Tenax TA	20/30 or 45/60	Supelco	10257	rest of trap

Old traps can be reused if unpacked carefully and cleaned and baked out properly. Use a glass wool puller to remove the wool plugs, and gently tap the sorbent out onto a piece of paper. If necessary, use the other end of the puller to loosen the sorbent bed, being careful not to scratch the inside of the trap. Discard the old sorbent. Rinse the empty trap with methanol, then bake in a GC oven for 30 minutes at 150°C.

The total length of the adsorbent bed is 12 to 13cm. You want to leave 2 to 3cm of space above the top of the last glass wool layer to ensure that all of the material is within the heated zone of the AutoCan trap heater.

With clean hands (no lotion!) place a small amount of glass wool, about 10-15mg, into the top of the trap and work it in with a piece of wire or tubing. Then use the trap packing tool (the larger steel rod that just barely fits inside the trap) to hold the plug in the trap while you pull away any loose strands of wool. Then use the long steel tube to push the plug down about 15cm. The idea is to keep the plug very compact, so it is a good idea to use the trap packing tool to push up from the bottom while pushing the wool in from the top, meeting 15cm down. The plug should not move too easily when pushed.

Weigh out the first sorbent (Carbosieve SIII) on weighing paper using the analytical balance. Using the glass funnel and a short piece of silicone tubing, pour the sorbent into the top of the trap. Tap on counter to get it all out of the funnel, then remove the funnel and tap some more to settle the sorbent into a compact bed. It is very important that there are no air spaces in the bed. However, it is also very important not to compress the sorbents too much, so be very careful when placing the glass wool plugs.

Place a glass wool plug on top of the first bed, starting as described above for the first plug. Push it gently onto the top of the sorbent with very little pressure.

Proceed with the other three packings in the table above (Carbosieve G, Carbopack Z, and Tenax TA).

After placing the last glass wool plug on top, turn the trap over and gently tap it on a piece of white paper to see if any sorbent comes out. If it does, you need to add more glass wool.

Now the trap needs to be conditioned in the trap heater. The sorbent manufacturers recommend that they be conditioned at succeedingly higher temperatures, with the final temperature being about 20-30˚C higher than the desorb temperature. The reason is that the sieves hold a lot of air and moisture and it is better to drive these off at lower temperatures to avoid damage to the material, such as cracking and oxidation which creates active sites. The temperatures and times are:

80˚C for 30 minutes, 50 to 100ml/min nitrogen or helium flow
200˚C for 30 minutes
265˚C for at least 3 hours

These temperatures are set using the variable power controller and thermocouple meter. Repeat for the other temperatures (low to high). Make sure the gas toggle valve in back is open, and measure flow at the top of the trap.