METHOD FOR THE DETERMINATION OF

VOLATILE PETROLEUM HYDROCARBONS (VPH) BY GAS CHROMATOGRAPHY/PHOTOIONIZATION DETECTOR/FLAME IONIZATION DETECTOR

Massachusetts Department of Environmental Protection

Bureau of Waste Site Cleanup

Commonwealth of Massachusetts

Executive Office of Energy and Environmental Affairs
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Commissioner

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Revision 2.1

Important Notice!

The purpose of this method is to provide data to help characterize the risks posed by petroleum-contaminated media. Innovative provisions and data adjustment steps are incorporated into the method to ensure that, in most cases, the resultant data will be moderately (but not overly) conservative (i.e., health protective). ***It is essential that all of the provisions and unique procedures in this method are understood and carefully implemented as written.*** Of particular note are the following:

Peak Integration Techniques:

- For individual Target VPH Analytes, the peaks from the PID are individually integrated (valley to valley). This applies to samples and standards.
- For the collective ranges of aliphatic hydrocarbons (i.e., C_5-C_8 and C_9-C_{12}), the chromatogram from the FID is continuously integrated (to baseline) between specified range "marker" compounds (e.g., n-pentane to n-nonane for C_5-C_8 aliphatic hydrocarbons). This applies to samples only; see Calibration Approach for peak integration techniques associated with calibration standards.
- For the collective range of C_9-C_{10} Aromatic Hydrocarbons, the chromatogram from the PID is continuously integrated (to baseline) between specified range "marker" compounds (i.e., o-xylene to naphthalene). This applies to samples only; see Calibration Approach for peak integration techniques associated with calibration standards.
- For the surrogate standard, the peak is individually integrated (valley to valley), so that the area can be subtracted from the collective areas of the hydrocarbon ranges discussed above. NOTE: if the method recommended surrogate (2,5-dibromotoluene) is utilized, this subtraction will not be required since this surrogate elutes after all aliphatic and aromatic compounds of interest.

Calibration Approach:

- The calibration factors (CFs) for the aliphatic hydrocarbon ranges are based on the correlation of collective FID area counts to the collective concentration values of a specified mixture of aliphatic hydrocarbon standards, in which the collective FID area count is determined via the summation of individual valley-to-valley peaks for the individual standards.
- For the aromatic range (i.e., C_9-C_{10} Aromatic Hydrocarbons), the CF is based on the correlation of the PID area count of one compound (1,2,4-trimethylbenzene) to the concentration value of this compound, in which the area count is determined via the individual valley-to-valley peak for this one compound.

  As such, the integration procedure for calibration (i.e., valley-to-valley of individual calibration standards) is different from the integration procedure for samples (i.e., integration to baseline across a specified range of the FID or PID chromatogram). This is necessary to ensure a conservative bias (i.e., an integration-to-baseline approach for the calibration standards would incorporate baseline "noise" which could lead to inappropriately elevated CF values resulting in inappropriately lower sample concentration levels which would not be health-protective).

Data Adjustments:

A series of steps are specified to calculate the final sample data results, to ensure that these values are not overly conservative, due to the addition of surrogate standards, and/or the "double counting" of analytes. This involves the subtraction of area counts and/or the subtraction of media concentration values (i.e., µg/L for aqueous samples or µg/kg for soil/sediment samples):

- When determining the collective area count for a specified hydrocarbon range (i.e., C_5-C_8 or C_9-C_{12} Aliphatic Hydrocarbons or C_9-C_{10} Aromatic Hydrocarbons), it is necessary to subtract the individual (valley-to-valley) peak area of any surrogate standards that elute within that range, if applicable.

- The individual PID concentrations of the Target VPH Analytes must be subtracted from the C_5 to C_8 and C_9 to C_{12} Aliphatic Hydrocarbon FID concentrations, and the PID concentration of C_9-C_{10} Aromatic Hydrocarbons must be subtracted from the FID concentration of C_9-C_{12} Aliphatic Hydrocarbons.

Significant Updates/Changes in Method Revision 2.1

This method revision (2.1) replaces revision 1.1 of the MassDEP VPH by GC/PID/FID test method, which was issued in May 2004. These updates and changes are relatively minor in nature, and are summarized below

Technical Revisions:

- Section 6.1.1.2: Recommended traps are provided and a requirement has been added to specify the trap used in the data package. If a different trap is used, the laboratory must perform a trap desorption efficiency study using a neat gasoline standard and the RPDs of each hydrocarbon range and Target VPH Analyte between the recommended trap and the trap utilized must be ≤25.
- Section 7.5.1: More flexibility was added for the volume of surrogate to be added to aqueous and solid samples.
- Section 9.1.2: MassDEP has added in a preference for the use of purge-and-trap autosamplers over manual load purge-and trap systems.
- Section 9.1.2.2: Details regarding the procedures for spiking of surrogates and matrix spike solutions in aqueous and solid samples prior to purge-and-trap have been added to the method.
- Section 9.1.3.7: A caution from the VPH PID/FID CAM Protocol (2010, et seq.) was added to the method regarding the amount of methanol extract to be added to reagent water. Section 9.3.6 and Table 5: The retention time windows were updated slightly to be consistent with the new VPH by GC/MS method and the APH method.
    - The ending marker for C_5-C_8 aliphatics is 0.01 minutes before nonane instead of 0.1 minutes.
    - The beginning marker for C_9-C_{12} aliphatics is 0.01 minutes before nonane instead of 0.1 minutes.
- Section 9.4.2.12: The %RSD for Target VPH Analytes and the surrogate in the initial calibration must be ≤20 (previously was ≤25).
- Section 9.4.2.13: A requirement from the VPH PID/FID CAM Protocol (2010, et seq.) was added to the method regarding the evaluation of the low standard when linear regression is used.
- Sections 9.4.2.15 and 10.2.2:
    - A requirement from the VPH PID/FID CAM Protocol (2010, et seq.) was added to the method regarding the analysis of an ICV.
    - The ICV acceptance criteria are 70-130% for each Target VPH Analyte and hydrocarbon range (was 80-120% in the 2010 CAM protocol).
- Section 9.4.3.5: The %D for Target VPH Analytes and the surrogate in the continuing calibration must be ≤20 (previously was ≤25).
- Section 10.2.6: Details were added regarding appropriate corrective actions when the LCS recoveries are outside of the acceptance criteria.
- Section 10.3.1: Details were added regarding appropriate corrective actions when the matrix duplicate RPDs are outside of the acceptance criteria.
- Section 11.3.1.4: A new significant modification was added regarding the use of non-linear regression during calibration.
- Section 11.3.3: The laboratory is required to include information on the column and trap used in the CAM deliverable.

Clarifications:

- "Important Notice" added at the beginning of the method to clarify proper peak integration during calibration and sample quantitation and data adjustment steps during sample quantitation.
- Sections 9.4.2.7 – 9.4.2.9: clarified that individual peak areas should be utilized for integration during calibration of the hydrocarbon ranges.
- Section 9.6.2: More details were added regarding the quantitation of the hydrocarbon ranges in samples.
- Section 11.3.3: Clarification on reporting of re-analyses and dilutions was added.

- Appendix 2: Updated chromatograms were added.
- Appendix 3:
    - Required VPH Data Report form updated to include prompts for the column and trap information.
    - MassDEP Analytical Protocol Certification Form updated to include both VPH method options (GC/MS and PID/FID).

MassDEP VPH by GC/MS

MassDEP has developed and published two analytical testing methods to quantify the concentrations of Volatile Petroleum Hydrocarbons (VPH) in aqueous and solid matrices. The first VPH method was issued in 1998 and involves the use of in-series photoionization and flame ionization detectors (PID and FID). This document constitutes the second revision of that method, which is now referred to as the "VPH by GC/PID/FID" method.

In January 2017, MassDEP issued a second VPH method that involves the use of a mass spectrometer, which s referred to as the "VPH by GC/MS" method. It is available at https://www.mass.gov/guides/compendium-of-analytical-methods-cam-massdep-bwsc

For additional information and insights on the origin and implications of the various requirements and biases within these methods, see "Evaluation of MassDEP Volatile Petroleum Hydrocarbon (VPH) Methods" at http://www.mass.gov/eea/docs/dep/cleanup/evaluation-of-vph-methods-june-2016.pdf.

LIST OF ACRONYMS

APH	Air-Phase Petroleum Hydrocarbons
ASTM	American Society for Testing and Materials
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CAM	Compendium of Analytical Methods
CF	Calibration Factor
%D	Percent Difference
DF	Dilution Factor
FID	Flame Ionization Detector
GC	Gas Chromatography
GC/MS	Gas Chromatography / Mass Spectrometry
HCl	Hydrochloric Acid
ICV	Initial Calibration Verification
I.D.	Internal Diameter
IDLC	Initial Demonstration of Laboratory Capability
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
LMB	Laboratory Method Blank
MassDEP	Massachusetts Department of Environmental Protection
MCP	Massachusetts Contingency Plan
MDL	Method Detection Limit
MTBE	Methyl tertiary butyl ether
NAPL	Non-aqueous Phase Liquid
OSHA	Occupational Safety & Health Administration
PID	Photoionization Detector
QC	Quality Control
%R	Percent Recovery
r	Correlation Coefficient
RL	Reporting Limit
RPD	Relative Percent Difference
%RSD	Percent Relative Standard Deviation
Rt	Retention Time
SOP	Standard Operating Procedure
SSB	System Solvent Blank
TSP	Trisodium Phosphate Dodecahydrate
VOC	Volatile Organic Compound
VPH	Volatile Petroleum Hydrocarbons

NOTE: Abbreviations of units (e.g., mL, mm, min, ºC, g, µL, µg/mL, µg/Kg, m, µm, µg/L, mg/Kg, ng, etc.) are not included.

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MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION (MassDEP)

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil/sediment matrices. Volatile aliphatic hydrocarbons are collectively quantitated within two carbon number ranges: C_5 through C_8 and C_9 through C_{12}. Volatile aromatic hydrocarbons are collectively quantitated within the C_9 to C_{10} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C (n-pentane) and 220°C (naphthalene).

1.2 This method is based on a purge-and-trap, gas chromatography (GC) procedure using a photoionization and flame ionization detector (PID/FID) in-series. This method should be used by, or under the direct supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.3 This method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection (MassDEP) to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MassDEP, 1994 and MassDEP, 2003). It is intended to produce data in a format suitable for the characterization of risk at sites undergoing evaluation under the Massachusetts Contingency Plan (MCP, 310 CMR 40.0000) using the aforementioned toxicological approach.

1.4 This method is one of two analytical options provided by MassDEP to collectively quantitate ranges of volatile aliphatic and aromatic hydrocarbons in aqueous and soil/sediment matrices. The other option was issued by the agency in January 2017, and involves the use of a mass spectrometer. The method detailed in this document is identified as "MassDEP VPH by GC/PID/FID." The other option is identified as "MassDEP VPH by GC/MS." MassDEP has also issued the "Method for the Determination of Air-Phase Petroleum Hydrocarbons (APH)" which enables the quantification of aliphatic and aromatic ranges of petroleum hydrocarbons and target analytes in air and vapor samples by gas chromatography/mass spectrometry (GC/MS).

1.5 In addition to the quantification of aliphatic and aromatic hydrocarbon ranges, the MassDEP VPH by PID/FID method is also designed to quantify the individual concentrations of the Target VPH Analytes benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and methyl tertiary butyl ether (MTBE) in aqueous and soil/sediment matrices. Use of this method to identify and quantify these Target VPH Analytes is optional.

1.6 Petroleum products suitable for evaluation by this method include gasoline, as well as the volatile fractions of mineral spirits, kerosene, #2 diesel fuel oil, jet fuels, and certain petroleum naphthas. This method, in and of itself, is not suitable for the evaluation of kerosene, jet fuel, heating oils, lubricating oils, and/or other petroleum products which contain a significant percentage of hydrocarbons heavier than C_{12} or with boiling points > 220°C.

1.7 The Reporting Limit (RL) of this method for each of the Target VPH Analytes is determined by the concentration of the lowest applicable calibration standard. The nominal RL for the individual target analytes is compound-specific, and ranges from approximately 0.050 to 0.25 mg/kg in soil/sediment matrices and 1 to 5 µg/L in aqueous matrices. The RLs for the collective hydrocarbon ranges are approximately 5-10 mg/kg in soil/sediment matrices and approximately 100-150 µg/L in aqueous matrices.

1.8 This method includes a series of data adjustment steps to determine the concentrations of the collective aliphatic and aromatic hydrocarbon ranges of interest. These steps may be taken by the laboratory or by the data user.

1.9 Data reports produced using this method must contain all of the information presented in Appendix 3. The format of these reports is left to the discretion of the individual laboratories (but must include the same certification statement presented in the aforementioned Appendix and must be provided in a clear, concise, and succinct manner). However, the format of the Laboratory Certification must follow the format presented in Appendix 3.

1.10 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of Target VPH Analytes, in that non-targeted hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantified as a Target VPH Analyte. Confirmatory analysis by a GC/MS procedure or other suitable method is recommended in cases where a Target VPH Analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where co-elution of a non-targeted hydrocarbon compound is suspected.

1.11 The first draft of this method was evaluated by two inter-laboratory "Round Robin" testing programs. In the final evaluation effort, participating laboratories were provided (single-blind) sand samples spiked with gasoline, and a "real world" groundwater sample contaminated by gasoline. Laboratory proficiency was evaluated using a Z-score approach. Data received from 21 laboratories performing this method without significant modifications are summarized below:

Matrix	# Labs Proficient	% Labs Proficient	Data from Proficient Laboratories		
			Fraction	%RSD	% labs within +/- 30% mean value
soil	20	95	C_5-C_8 Aliphatics	28	80
			C_9-C_{12} Aliphatics	52	50
			Total GC/FID	31	70
			C_9-C_{10} Aromatics	24	80
water	17	81	C_5-C_8 Aliphatics	31	71
			C_9-C_{12} Aliphatics	44	47
			Total GC/FID	24	76
			C_9-C_{10} Aromatics	20	82

Laboratory and method performance were believed to have been adversely impacted by the use of multiple chromatographic columns, which may have significantly altered the placement of aliphatic hydrocarbons into either the C_5-C_8 or C_9-C_{12} Aliphatic Hydrocarbon ranges. Better performance was noted for the aromatic fraction and total GC/FID data. Improvements incorporated into this final method are expected to significantly improve overall method performance.

1.12 The VPH by GC/PID/FID and VPH by GC/MS methods are two ways to quantify collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons within specified carbon number ranges. Both have been designed in a manner that attempts to strike a reasonable balance between analytical method performance and utility. In this manner, assumptions and biases have been structured into the methods to help ensure protective, though not overly conservative data.

As an example, MassDEP recognizes that branched alkanes have lower boiling points than their n-alkane counterpart, while many of the cycloalkane constituents of gasoline range volatile organics have higher boiling points than their n-alkane counterpart. As a consequence:

(1) Depending upon the specific chromatographic column used, most branched C_9 alkanes are expected to elute before n-nonane, the beginning marker compound for the C_9 through C_{12} aliphatic hydrocarbon range, and will be conservatively counted in the more toxic C_5 through C_8 aliphatic hydrocarbon range;

(2) Depending upon the specific chromatographic column used, most branched C_5 alkanes will elute before n-pentane, the beginning marker compound for the C_5 through C_8 aliphatic hydrocarbon range, and will therefore not be counted in the C_5 through C_8 aliphatic hydrocarbon range; and

(3) Depending upon the specific chromatographic column used, most cycloalkanes within the C_5 through C_8 and C_9 through C_{12} aliphatic hydrocarbon ranges will be counted within their proper range with the exception of some C_{12} cycloalkanes which will elute after naphthalene, the end marker compound for the C_9 through C_{12} aliphatic hydrocarbon range.

Based on the nature of petroleum releases encountered in the environment, the collective concentrations of the volatile aliphatic ranges as measured by the VPH Methods are considered to be suitable for the evaluation of the risks posed by these releases, consistent with the toxicological approach developed by MassDEP to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MassDEP, 1994 and MassDEP, 2003).

1.13 There may be better, more accurate, and/or less conservative ways to produce Target VPH Analyte and hydrocarbon range data. MassDEP encourages methodological innovations that (a) better achieve method and/or data quality objectives, (b) increase analytical precision and accuracy, (c) reduce analytical uncertainties and expenses, and/or (d) reduce the use of toxic solvents and generation of hazardous wastes.

All significant modifications to this method, however, must be disclosed and described on the data report form, as detailed in Section 11.3 and the MassDEP Analytical Protocol Certification Form (See Appendix 3, Exhibit 2, Question E). Laboratories that make such modifications, and/or develop and utilize alternative approaches and methods, are further required to demonstrate that:

- Such modifications or methodologies adequately quantify the petroleum hydrocarbon ranges, as defined in Sections 3.6 through 3.8 of this document, ensuring that any methodological uncertainties or biases are addressed in a manner that ensures protective (i.e., conservative) results and data (e.g., over, not under-quantification of the more toxic ranges);

- Such modifications and/or methodologies employ and document initial method demonstration and ongoing quality control (QC) procedures consistent with approaches detailed in the MassDEP Compendium of Analytical Methods (CAM); and

- Such methods and procedural modifications are fully documented in a detailed standard operating procedure (SOP).

1.14 Additional information and details on the MassDEP VPH approach are available at http://www.mass.gov/dep/cleanup/laws/policies.htm#vph.

1.15 This method should be used in conjunction with the current version of CAM IV A, "Quality Control Requirements and Performance Standards for the Analysis of Volatile Petroleum Hydrocarbons (VPH) by Gas Chromatography/Photoionization Detector/Flame Ionization Detector in Support of Response Actions Under the Massachusetts Contingency Plan (MCP)". WSC-CAM-IV A was developed by MassDEP to complement this MassDEP VPH by GC/PID/FID Method and to provide more detailed guidance regarding compliance with the QC requirements and performance standards of the MassDEP VPH by GC/PID/FID Method.

2.0 SUMMARY OF METHOD AND DATA QUALITY OBJECTIVES

2.1 Samples are analyzed using purge-and-trap sample concentration. The GC is temperature programmed to facilitate separation of the individual compounds and hydrocarbon ranges of interest on a capillary column. All compounds are detected using a PID and FID in series. Quantitation is based on comparing the PID and FID response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The PID chromatogram is used to determine the individual concentrations of Target VPH Analytes (BTEX/MTBE/naphthalene) and collective concentration of aromatic hydrocarbons within the C_9 through C_{10} range. The FID chromatogram is used to determine the collective concentration of aliphatic hydrocarbons within the C_5 through C_8 and C_9 through C_{12} ranges.

2.2 This method is suitable for the analysis of aqueous samples, soils, sediments, wastes, sludges, and non-aqueous phase liquid (NAPL) samples. However, it should be noted that the method was validated only for soil and aqueous matrices. Aqueous samples may be analyzed directly for VPH by purge-and-trap concentration and GC/PID/FID. Soil/sediment samples are dispersed in methanol to dissolve the volatile organic constituents. An aliquot of the methanol extract is then analyzed by purge-and-trap concentration and GC/PID/FID.

2.3 This method is based on (1) USEPA Methods 5030B, 5035A, 8000D, 8015C, and 8021B, SW-846, "Test Methods for Evaluating Solid Wastes," (2) Draft "Method for Determination of Gasoline Range Organics," EPA UST Workgroup, November, 1990; and (3) "Modified GRO Method for Determining Gasoline Range Organics," Wisconsin Department of Natural Resources, PUBL-SW-140, 1992.

2.4 Data Quality Objectives should be developed and applied for sampling and analytical efforts involving the use of this method. Key parameters of interest include: (a) the acceptability of RLs achievable by the laboratory for the contaminants of interest and (b) the identification and reporting of target analytes.

3.0 DEFINITIONS

3.1 **Aliphatic Hydrocarbons** are defined as acyclic or cyclic, saturated or unsaturated compounds that contain only carbon and hydrogen atoms, excluding aromatic compounds.

3.2 **Aromatic Hydrocarbons** are defined as compounds whose structures include a cyclic structure and a closed conjugated system of double bonds containing only carbon and hydrogen atoms.

3.3 **Analytical Batch** is defined as a group of field samples with similar matrices which are processed as a unit. For QC purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less is defined as a separate analytical batch.

3.4 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

3.5 **Continuing Calibration Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The continuing calibration standard is prepared from the same stock solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.6 **C_5 through C_8 Aliphatic Hydrocarbons** are defined as all aliphatic petroleum hydrocarbon compounds that elute from just before n-pentane (C_5) to just before n-nonane (C_9). C_5 through C_8 aliphatic hydrocarbons are determined using the FID.

3.7 **C_9 through C_{12} Aliphatic Hydrocarbons** are defined as all aliphatic petroleum hydrocarbon compounds that elute from just before n-nonane (C_9) to just before naphthalene. C_9 through C_{12} aliphatic hydrocarbons are determined using the FID.

3.8 **C_9 through C_{10} Aromatic Hydrocarbons** are defined as all aromatic petroleum hydrocarbon compounds that elute from just after o-xylene to just before naphthalene; therefore this range will include any unsaturated hydrocarbons (e.g., alkenes, alkynes, carbonyls, ethers, etc.). Although naphthalene is an aromatic compound

with 10 carbon atoms, it is excluded from this range because it is evaluated as a separate Target VPH Analyte. C_9 through C_{10} aromatic hydrocarbons are determined using the PID.

3.9 **Field Duplicates** are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.10 **Laboratory Control Sample (LCS)** is defined as a reagent water blank (when associated with aqueous samples) or clean methanol blank (when associated with soil/sediment samples) fortified with the matrix spiking solution. The LCS is prepared and analyzed in the same manner as a sample and its purpose is to determine the bias of the analytical method.

3.11 **Laboratory Control Sample Duplicate (LCSD)** is defined as a reagent water blank (when associated with aqueous samples) or clean methanol blank (when associated with soil/sediment samples) fortified with the matrix spiking solution. The LCSD is prepared separately from the LCS but is prepared and analyzed in the same manner as the LCS. The purpose of LCS duplicates is to determine the bias and precision of the analytical method.

3.12 **Laboratory Method Blank (LMB)** is defined as an aliquot of reagent water (when associated with aqueous samples) or clean methanol (when associated with soil/sediment samples) spiked with a surrogate standard. The laboratory method blank is prepared and analyzed in the same manner as a sample, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.13 **Matrix Duplicates** are defined as split samples prepared and analyzed separately with identical procedures. For soil/sediment samples, matrix duplicate samples are taken from the same sampling container. For aqueous samples, a separate container is used for the matrix duplicate sample. The analysis of matrix duplicates gives a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.14 **Matrix Spike Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The purpose of the matrix spike sample is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analysis of an unspiked sample aliquot. The measured values in the matrix spike sample must be corrected for background concentrations when calculating recoveries of spiked analytes.

3.15 **Matrix Spiking Solution** is defined as a solution prepared from a separate source than used for the calibration standards, containing known concentrations of method analytes.

3.16 **System Solvent Blank (SSB)** is defined as an aliquot of organic-free water (American Society for Testing and Materials [ASTM] Type I reagent grade) and purge-and-trap grade, or equivalent, methanol. For aqueous samples 4.0 uL of methanol is mixed with 5.0 mL of water and for soil/sediment samples 100 uL of methanol is mixed with 4.9 mL of water. The SSB is analyzed in the same manner as a sample, exposed to all glassware, solvents, reagents, and equipment. Surrogates must not be spiked into SSBs. An SSB provides one way of determining the level of noise and baseline rise attributable solely to the analytical system, in the absence of any other analytes or non-analytical related contaminants.

3.17 **Target VPH Analytes** are defined as benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, naphthalene, and MTBE.

3.18 **Unadjusted C_5 through C_8 Aliphatic Hydrocarbons** are defined as all petroleum hydrocarbon compounds which elute on the FID chromatogram from n-pentane (C_5) to just before n-nonane (C_9).

3.19 **Unadjusted C_9 through C_{12} Aliphatic Hydrocarbons** are defined as all petroleum hydrocarbon compounds which elute on the FID chromatogram from just before n-nonane (C_9) to just before naphthalene.

3.20 **Volatile Petroleum Hydrocarbons (VPH)** are defined as collective fractions of hydrocarbon compounds eluting from n-pentane to just before naphthalene, excluding Target VPH Analytes. VPH is comprised of C_5 through C_8 Aliphatic Hydrocarbons, C_9 through C_{12} Aliphatic Hydrocarbons, and C_9 through C_{10} Aromatic Hydrocarbons.

3.21 **Volatile Petroleum Hydrocarbon (VPH) Component Standard** is defined as a 15 component mixture of the aliphatic and aromatic compounds and one surrogate listed in Table 1. The compounds comprising the VPH Component Standard are used to (a) define the individual retention times and calibration factors for each of the Target VPH Analytes, (b) define and establish the retention time windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average calibration factors or generate calibration curves that can in turn be used to calculate the collective concentrations of hydrocarbons within these ranges.

3.22 All other terms are as defined in the most current version of SW-846, "Test Method for Evaluating Solid Waste," USEPA.

4.0 INTERFERENCES AND METHOD LIMITATIONS

4.1 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage or by dissolution of volatiles into the methanol used for preservation. Trip blanks prepared from both reagent water (when associated with aqueous samples) and methanol (when associated with soil/sediment samples) should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.2 Cross-contamination can occur whenever a low-concentration sample is analyzed immediately after a high-concentration sample. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling-point compounds or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water, and then dry in an oven at 105°C between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of an SSB or LMB to check for cross-contamination. However, due to the potential for samples to be analyzed using an autosampler, the ability to perform this blank analysis may not always be possible. If the sample analyzed immediately after the unusually concentrated sample is free from contamination, then the assumption can be made that carryover or cross-contamination is not an issue. However, if this sample did detect analytes which were present in the unusually concentrated sample, reanalysis is required for all samples analyzed after this highly concentrated sample which detected similar analytes.

4.3 The response selectivity of a PID is used in this method to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. All compounds eluting on the PID chromatogram after o-xylene are identified by the method as aromatic hydrocarbons. This will lead to an overestimation of aromatic hydrocarbons within samples, as certain aliphatic compounds will elicit a response on the PID, particularly unsaturated compounds such as alkenes. The significance and implications of this overestimation will vary from sample to sample; where less conservative data are desired, additional actions should be considered to minimize the detection of non-aromatic compounds, including the use of a lower energy PID lamp and/or an alternative chromatographic column.

4.4 Certain organic compounds not associated with the release of petroleum products including chlorinated solvents, ketones, and ethers may be detected by this method and may contribute to the collective response quantified within an aliphatic or aromatic hydrocarbon range.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method have not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of Occupational Safety & Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of safety data sheets should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 Purge-and-Trap System

6.1.1 The purge-and-trap system consists of a sample purging chamber, a concentrating trap, and a thermal desorber. Complete systems are available commercially.

6.1.1.1 The purging chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. Purging devices larger than 5 mL have a reduced purging efficiency and should not be used. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. Fritted glass or needle sparge cells may be used. If needle sparge cells are used, the purge gas must be introduced no more than 5 mm from the base of the water column. Alternate sample purging devices may be used, provided an equivalent performance is demonstrated.

6.1.1.2 The recommended trap should be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap should be packed with 400 mg of Carbopack B (Supelco Cat. No. 2-0273). Alternative trap packing materials include: 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat No. 2-0321); or 7.7 cm Carbopack C and 1.2 cm Carbopack B (Supelco Cat No. 2-1064). In general, Carbopack trap packing materials are recommended because they have less of a tendency to retain methanol, which could interfere with the elution of pentane and quench the FID flame. The recommended trap length and packing materials may be varied as long as equivalent performance (i.e., meeting QC criteria of method) has been verified.

NOTE: Based upon data obtained from the MassDEP VPH by GC/MS Method Round Robin testing program, the choice of traps may have a significant impact on the quantification of aliphatic and aromatic compounds within the collective hydrocarbon ranges specified in the method, specifically the heavier boiling point components. It must be demonstrated that the selected trap has equivalent properties for the efficient desorption of the aliphatic and aromatic compounds and ranges of interest. In all cases, the laboratory must specify the trap used in the data package (see Appendix 3).

To demonstrate equivalency of trap desorption efficiency, a neat gasoline standard must be analyzed using a trap with the recommended packing materials and the proposed substitute trap, with all other run and system parameters held constant. The concentrations of C_5-C_8 and C_9-C_{12} aliphatic hydrocarbons, C_9-C_{10} aromatic hydrocarbon ranges, and Target VPH Analytes must be determined for each trap. The relative percent differences (RPDs) between the concentrations of each hydrocarbon range and Target VPH Analyte obtained from each trap must be ≤ 25.

6.1.1.3 The traps should be conditioned and desorbed according to the manufacturer's guidelines. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

6.1.1.4 The desorber should be capable of rapidly heating the trap to the temperature recommended by the trap manufacturer prior to the beginning of the flow of desorption gas.

6.2 Gas Chromatograph System

6.2.1 An analytical system complete with a temperature programmable GC for use with a capillary column is required.

6.2.2 Chromatographic Column: The required column is: 105 m x 0.53 mm internal diameter (I.D.) Restek RTX-502.2 with 3 micron film thickness, or column with equivalent chromatographic properties.

NOTE: Based upon data obtained from the MassDEP VPH by GC/PID/FID Method 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 collective hydrocarbon 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. In all cases the laboratory must specify the column used in the data package (see Appendix 3).

To demonstrate equivalency of column chromatography, a neat gasoline 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 C_5-C_8 and C_9-C_{12} aliphatic hydrocarbons, C_9-C_{10} aromatic hydrocarbons, and Target VPH Analytes must be determined for each column (in which the PID concentrations of the Target VPH Analytes have been subtracted from the FID concentrations of the aliphatic hydrocarbon ranges). The RPDs between the concentrations of each hydrocarbon range and Target VPH Analyte obtained from each column must be $\leq$ 25. The elution order of VPH components on the proposed substitute column must be equivalent to the elution order on the required column.

6.3 Detectors

6.3.1 The method requires the use of a PID in series with a FID; the PID first in the series. The method is based upon the use of a 10.0 +/- eV PID lamp, although lower energy lamps are permissible in order to minimize PID response to aliphatic compounds. In lieu of an in-series arrangement, in-parallel PID and FID units may be also used if the RL for the method is not adversely affected.

6.3.2 A data station is required that is capable of storing and reintegrating chromatographic data and capable of determining peak areas using a forced baseline projection.

6.4 The following glassware is used in this method:

6.4.1 VOC Vials: Wide mouth 60-mL VOC vials or 40-mL VOC vials with Teflon/silicone septa for soil/sediment matrices; 40-mL VOC vials with Teflon/silicone septa for aqueous matrices.

6.4.2 Class "A" Volumetric flasks: 10-mL, 50-mL, 100-mL, and 1,000-mL with ground-glass stoppers.

6.5 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards, if required. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil/sediment samples.

6.6 Ultrasonic bath.

6.7 Disposable pipets: Pasteur.

6.8 Syringes: 5-mL Luerlock glass hypodermic and 5-mL gas-tight syringe with shutoff valve.

6.9 Syringe valve: Two-way, with luer-lock connections.

6.10 Microsyringes: 1-µL, 5-µL, 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL.

6.11 Spatula: Stainless steel.

6.12 Drying oven.

6.13 Dessicator.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent Water: organic-free water (ASTM Type I reagent grade water).

7.1.2 Solvent: methanol; purge-and-trap grade or equivalent. Store away from other solvents.

7.2 Stock Standard Solution

Prepare stock standard solutions in methanol at approximately 10 micrograms per microliter (µg/µL), or purchase certified solutions. Preparation of stock standards and component standards should be done using volumetric glassware. The stock standard solution consists of the aliphatic and aromatic range calibration compounds and Target VPH Analytes listed in Table 1. A separate stock standard solution containing only the surrogate must be prepared. Transfer the stock standard solution into a Teflon-lined screw-cap or crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light. Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.3 Primary Dilution Standard

Using the stock standard solutions, prepare primary dilution standards in methanol, as needed. The primary dilution standards should be prepared at 100 µg/mL. These standards should be stored with minimal headspace, at -10°C to -20°, and should be checked frequently for signs of degradation or evaporation. The primary dilution standards should be replaced at least monthly.

7.4 VPH Calibration Standards

Prepare VPH Calibration standards in reagent water from the primary dilution standards (in methanol). At a minimum, five different concentrations are required for a valid calibration curve. The calibration concentrations must be evenly dispersed over the full working range of the detector with the lowest calibration point corresponding to the RL. The highest concentration defines the maximum upper working range of the calibration curve. Target VPH analytes may not be reported above this concentration without sample dilution. Tables 2a and 2b provide recommended concentrations for each calibration standard for a 5-point initial calibration of hydrocarbon ranges, Target VPH Analytes, and the surrogate.

<u>Aqueous standards are not stable and should be discarded after one hour.</u>

7.5 Surrogate Standard

The analyst must monitor both the performance of the analytical system and the effectiveness of the method in dealing with sample matrices by spiking each sample, LMB, LCS, LCSD, and matrix spike with a surrogate standard. The surrogate standard is included in the VPH calibration standards. The recommended surrogate standard is 2,5-dibromotoluene, which elutes after all aliphatic and aromatic compounds of interest.

However, other surrogates may be used as long as they are adequately resolved from the components of interest.

7.5.1 Recommended Surrogate Spiking Solution: From a stock standard solution, prepare a surrogate spiking solution in methanol. Add a specified volume (recommended 5-10 µl) of this surrogate spiking solution directly into the 5-mL syringe with every aqueous sample, LMB, LCS, LCSD, and matrix spike in order to yield a final concentration of 50 µg/L. Add a specified volume (recommended not to exceed 1.0 mL) of the surrogate spiking solution to soil/sediment samples during the extraction step (See Section 9.1.3.2) in order to yield a final concentration of 2.5 mg/kg (or 50 µg/L on column). The use of higher concentrations is permissible and advisable when spiking highly contaminated samples.

7.6 Matrix Spiking Solution

The recommended matrix spiking solution, consisting of the full analyte list (VPH Component Standard), is prepared in methanol at a nominal concentration of 50 µg/mL.

7.7 Petroleum Reference Standard (To demonstrate equivalency of column chromatography and trap desorption efficiency)

The Petroleum Reference Standard consists of an API or commercial gasoline standard. Prepare Petroleum Reference Standard spiking solutions by accurately weighing approximately 0.0100 g of neat product. Dissolve the neat product in methanol and dilute to volume in a 100-mL volumetric flask.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Aqueous Samples

8.1.1 Aqueous samples should be collected in triplicate (or the number of vials directed by the laboratory) without agitation and without headspace in contaminant-free 40 mL glass VOC vials with Teflon-lined septa screw caps. The Teflon liner must contact the sample. All samples must be chemically preserved as follows (based on the laboratory's purge-and-trap system setup).

a. Samples analyzed with ambient purge temperature: Samples must be acidified to a pH of 2.0 or less at the time of collection. This can generally be accomplished by adding 3 or 4 drops (0.1 to 0.2 mL) of 1:1 hydrochloric acid (HCl) (1 part reagent water and 1 part concentrated HCl) to a 40-mL sample vial prior to collection. Samples must be cooled to 0-6°C immediately after collection.
b. Samples analyzed with heated purge temperature: Samples must be treated to a pH of 11.0 or greater at the time of collection. This can be accomplished by adding 0.40 to 0.44 grams of trisodium phosphate dodecahydrate (TSP) to a 40-mL sample vial prior to collection. Samples must be cooled to 0-6°C immediately after collection.

8.1.2 A chain-of-custody form must accompany all sampling vials and must document the date and time of sample collection and preservation method used. The pH of all water samples must be determined by the laboratory after sample analysis has been completed. The pH measurement may be performed on leftover sample. Any acid-preserved sample found to contain a pH above 2 must be so noted on the laboratory/data report sheet. Any TSP-preserved sample found to contain a pH <11 must be so noted on the laboratory data report sheet. Additional details and recommendations on aqueous sample preservation are provided in Appendix 4.

8.1.3 A reagent water trip blank, preserved in the same manner as the samples, should accompany each batch of water samples. Refer to WSC-CAM-VII A for the **required** frequency of trip blanks.

8.1.4 Any sample received by the laboratory that is not packed in ice or cooled to 0-6°C must be so noted on the laboratory/data report sheet. The temperature of the cooler must be recorded by the laboratory upon receipt.

8.1.5 Aqueous samples must be analyzed within 14 days of collection.

8.2 Soil/Sediment Samples

8.2.1 Soil/sediment samples must be collected in a manner that minimizes sample handling, environmental exposure and/or aeration. The use of specially designed air-tight collection samplers or a 30-mL plastic syringe with the end sliced off is recommended. All soil/sediment must be removed from the glass threads of the vial to ensure an adequate seal. Samples must be cooled to 0-6°C immediately after collection.

8.2.2 **Methanol preservation of soil/sediment samples is mandatory.** Methanol (purge-and-trap grade) must be added to the sample vial before or immediately after sample collection. In lieu of the in-field preservation of samples with methanol, soil samples may be obtained in specially-designed air tight sampling devices, provided that the samples are extruded and preserved in methanol within 48 hours of collection. Additional details and recommendations on soil/sediment sampling are provided in Appendix 4.

8.2.3 The desired ratio of methanol-to-soil/sediment is 1 mL methanol/1 gram soil/sediment, +/- 25%. The exact weight of the soil/sediment sample and volume of methanol must be known or ascertained by the laboratory when calculating and reporting soil/sediment concentration data. A recommended practice is for a laboratory to provide labeled, pre-weighed sampling vials with the measured volume of methanol clearly indicated to the field sampling technician. The laboratory "fill line" indicating the height of the methanol meniscus should be permanently marked on the side of the sampling container. After the soil/sediment sample is added to the methanol in the sampling container, the sample "fill line" indicating the height of the sample-displaced (increased) methanol level should also be marked by the field sampling technician. **In all cases, the soil/sediment sample in the vial must be completely covered by methanol.**

8.2.4 Samples for VPH analysis should be collected in duplicate 60-mL or 40-mL VOC vials with Teflon-lined septa screw caps. An additional sample of the soil/sediment must also be obtained (without methanol) to allow for a determination of moisture content and VPH dry weight correction factors. Refer to Appendix 5 for details on shipping methanol-preserved samples.

8.2.5 A methanol trip blank should accompany each batch of soil/sediment samples.

8.2.6 A chain-of-custody form must accompany all sampling vials and must document the date and time of sample collection and, where appropriate, the volume of methanol added. Observations of vial leakage must be so noted on the laboratory/data report sheet.

8.2.7 Any sample received by the laboratory that is not packed in ice or cooled to 0-6°C must be so noted on the laboratory/data report sheet. The temperature of the cooler must be recorded by the laboratory upon receipt.

8.2.8 Soil/sediment samples must be analyzed within 28 days of collection.

8.3 A summary of sample collection containers, preservation, and holding times is provided in Table 3.

9.0 ANALYTICAL PROCEDURE

9.1 Sample Preparation and Purging

9.1.1 It is highly recommended that all samples be screened prior to analysis. This screening step may be analysis of a soil/sediment sample's methanol extract (diluted), the headspace method (SW-846 method 3815), or the hexadecane extraction and screening method (SW-846 Method 3820). For soil/sediment samples, headspace screening of the unpreserved vial (obtained for the purposes of determining soil/sediment moisture content) is also an option.

9.1.2 Aqueous Samples

Introduce volatile compounds into the GC using a purge-and-trap concentrator.

Note: Although procedures for manual purge-and-trap load systems are provided below, MassDEP prefers the use of purge-and-trap autosamplers to reduce variability and to minimize the handling of samples for VPH analysis.

9.1.2.1 For a manual load system, remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40-mL vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

Alternatively, commercially-available autosamplers may be used to automatically introduce a 5.0 mL sample aliquot directly from a 40 mL sampling vial to the system for purging. The addition of surrogates may also be performed automatically by the autosampler. Follow manufacturer's instructions for operation. In some cases, concentrations of surrogates and/or matrix spikes may need to be modified to accommodate the fixed injection volumes associated with automated sample introduction systems.

If necessary, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay. If using an autosampler, sufficient volume of the diluted sample should be prepared to fill a 40 mL sampling vial. Analyze the diluted sample as described above.

9.1.2.2 Spiking Samples.

If the purge-and-trap manual load system is utilized:

- Add a specified volume (recommended 5-10 µL) of the surrogate spiking solution through the valve bore of the syringe to yield a final concentration of 50 µg/L. Close the valve.

- If matrix spike analysis is to be performed, add a specified volume (recommended 5-10 µL) of the matrix spiking solution through the valve bore of the syringe to yield a nominal concentration of 50 µg/L. Close the valve.

- Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber. Close the valve.

If the purge-and trap autosampler is utilized:

- The addition of surrogates may be performed automatically by the autosampler.

- If matrix spike analysis is to be performed, add a specified volume (recommended 5-10 µL) of the matrix spiking solution through the Teflon-lined septa screw cap of the VOC vial.

9.1.2.3 Regardless if manual load or autosampler is used, purge the sample for 11 minutes. Recommended purge-and-trap operating parameters are provided in Table 4. At the conclusion of the purge time, attach the trap to the GC (if necessary), adjust the device to the desorb mode, and begin the GC temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 260°C (desorb temperature) and backflushing the trap with inert gas between 15 and 20 mL/min for 4 minutes.

9.1.2.4 While the trap is desorbing into the GC, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of compounds into subsequent analyses.

9.1.2.5 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 260°C. After approximately 7 to 15 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. After a highly concentrated sample, a longer baking time may be necessary. When cool, the trap is ready for the next sample.

9.1.2.6 Following sample analysis, measure and record the pH of the remaining sample.

9.1.3 Soil/Sediment/Samples

Soil and sediment samples are extracted with methanol. An aliquot of the methanol extract is added to reagent water and volatile compounds are introduced into the GC using a purge-and-trap concentrator.

9.1.3.1 Weigh the sample vial to 0.1 g on a top-loading balance and determine the weight of the soil/sediment sample; this determination requires knowledge of the empty/tared weight of the sample vial and volume/weight of methanol preservative that was added to the sample vial.

9.1.3.2 Add a specified volume (recommended not to exceed 1.0 mL) of the surrogate spiking solution through the septum of the sample vial. The concentration and/or volume of the surrogate spiking solution may need to be increased for samples that are highly contaminated (based upon screening and/or field notes), to prevent dilution to below detectable limits. The amount of surrogate added should yield a final concentration of 2.5 mg/kg.

9.1.3.3 If matrix spike analysis is to be performed, add a specified volume (recommended not to exceed 1.0 mL) of the matrix spiking solution through the septum of a separate sample vial to yield a nominal concentration of 2.5 mg/kg.

9.1.3.4 Agitate sample to facilitate adequate mixing of spiking solution(s).

9.1.3.5 Allow soil/sediment to settle until a layer of methanol is apparent.

9.1.3.6 Using a microliter syringe, withdraw an appropriate aliquot of the methanol extract for sparging through the septum of the container. Sample screening data can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis.

9.1.3.7 Remove the plunger from one 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for addition of the extract (e.g., for 100 µL of extract adjust to 4.9 mL). Pull the plunger to 5.0 mL for addition of the sample extract. Add the volume of methanol extract determined from screening (recommended 100 µL if dilution not required). **Be advised that the volume of methanol aliquot added to the**

reagent water should not exceed 200 µL to preclude adverse solvent front and trap breakthrough difficulties. Alternatively, the addition of methanol extracts to reagent water can be performed in 40 mL VOC vials when an autosampler is used keeping similar methanol to water ratios.

9.1.3.8 If using a manual load purge-and-trap system, attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber. Close the valve.

9.1.3.9 Complete operations as specified in Sections 9.1.2.3 through 9.1.2.5.

9.1.4 Determination of Percent Moisture

9.1.4.1 Soil and sediment results must be reported on a dry-weight basis.

Transfer 5 to 10 g of sample into a tared (± 0.1 g) crucible. This sample must be obtained from a vial or container that does not contain methanol. Dry this 5 to 10 g sample overnight at 105°C, and reweigh (± 0.1 g). Allow to cool in a desiccator before reweighing. Calculate the percent moisture of the sample using the equation provided in Section 9.6.3 (Equation 10). Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.

9.2 Analytical Conditions

GC/PID/FID Conditions:

Chromatographic Column:	105 m x 0.53 mm I.D., 3.0 µm Restek Rtx- 502.2
Oven Temperature Program	Initial oven temperature 45°C, hold time 1 min; to 100 °C @ 3°C/min, hold time 0 min to 160°C @ 8 °C/min, hold time 0 min to 230 °C @ 20°C/min, hold time 7.5 min
Gas Flow Rates:	Carrier gas - Helium @ 12.5 mL/ min Oxidizer - Air @ 350 mL/min Fuel - Hydrogen @ 30 mL/min Make up - Air @ 17.5 mL/min
Injection Port Temperature:	250°C
Column Inlet Pressure:	20 p.s.i.g.
Detector Temperature:	230°C (PID) 230°C (FID)

9.3 Retention Time Windows

9.3.1 Before establishing retention time (Rt) windows, optimize the GC system's operating conditions. Make three injections of the VPH Component Standard over the course of a 72-hr period. Serial injections over less than a 72-hr period may result in Rt windows that are too restrictive.

9.3.2 Calculate the standard deviation of the three absolute Rts for each individual compound in the VPH Component Standard.

9.3.3 The Rt window is defined as plus or minus three times the standard deviation of the absolute Rt for each compound in the VPH Component Standard. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.4 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a representative statistically-derived Rt window.

9.3.5 The laboratory must calculate Rt windows for each compound in the VPH Component Standard on each GC column and whenever a new GC column is installed. These data must be retained by the lab.

9.3.6 The Rt window of the C_5-C_8 aliphatic hydrocarbons is defined as beginning 0.1 minutes before the elution of n-pentane and ending 0.01 minutes before the elution of nonane. The C_9-C_{12} aliphatic hydrocarbon range begins 0.01 minutes before the elution of nonane; therefore there is no overlap of the two ranges and the nonane peak is only included in the C_9-C_{12} aliphatic hydrocarbon range. The C_9-C_{12} aliphatic hydrocarbon range ends 0.1 minutes before the elution of naphthalene.

The Rt window for the C_9-C_{10} aromatic hydrocarbons is defined as beginning 0.1 minutes **after** the elution of o-xylene and ending 0.1 before the elution of naphthalene.

VPH marker compounds and windows are summarized in Table 5.

9.4 Calibration

9.4.1 The VPH calibration standards are used to calibrate the GC/PID/FID system. Two distinct calibration operations are necessary.

9.4.1.1 Target VPH Analytes and Surrogate: Calibration Factors (CFs) are calculated for the Target VPH Analytes and surrogate standard, based upon a correlation between the concentration of analyte/surrogate and PID area counts for the analyte/surrogate peaks. This allows for the individual identification and quantitation of these specific compounds. It is not necessary to develop CFs for any other individual VPH Components.

9.4.1.2 Collective Aliphatic/Aromatic Hydrocarbon Ranges: CFs are calculated for C_5-C_8 aliphatic hydrocarbons and C_9-C_{12} aliphatic hydrocarbons based upon a correlation between the TOTAL concentration of aliphatic VPH Components eluting within the range of interest and the total FID area count of the applicable VPH component peaks. A CF is calculated for C_9-C_{10} aromatic hydrocarbons based upon a correlation between the concentration of the one aromatic VPH Component used to calibrate this range and the PID area count of this VPH component. Specified VPH Components are designated marker compounds to define the beginning and end of the hydrocarbon ranges (see Table 5). A listing of the hydrocarbon range compounds used to establish CFs for each hydrocarbon range of interest and their individual component concentration (µg/L) is provided in Table 2b.

9.4.2 Initial Calibration

9.4.2.1 Initial calibration is performed at instrument set-up and at any time recalibration is required or performed.

9.4.2.2 The use of CFs is the preferred approach to determine the relationship between the detector response and the Target VPH Analyte and hydrocarbon range concentrations. It is also permissible to utilize linear regression (see Sections 9.4.2.12 and 9.4.2.13). The linear regression approach for Target VPH Analytes and hydrocarbon ranges is described in Appendix 6. The use of non-linear regression is not allowed in this method and is considered a significant modification as discussed in Section 11.3.1.

9.4.2.3 An initial calibration is performed using a minimum of five different concentrations of VPH calibration standards as per Section 7.4. Recommended Target VPH Analyte and hydrocarbon range calibration standard concentrations are provided in Tables 2a and 2b, respectively. The calibration concentrations must be evenly dispersed over the full working range of the detector with the lowest calibration point corresponding to the target

RL for the Target VPH Analytes (see Section 12.0). NOTE: If an autosampler is used to spike the surrogate in calibration standards, five standards with the same concentration of surrogate are acceptable for determination of a CF for the surrogate.

9.4.2.4 Analyze each VPH Calibration standard according to the procedures specified in Sections 9.1 and 9.2.

9.4.2.5 Target VPH Analytes and Surrogate - Tabulate the PID area response against the concentration for each Target VPH Analyte and surrogate, and calculate a CF for each compound using Equation 1. Perform this calculation for each Target VPH Analyte and the surrogate.

Equation 1: Calibration Factor for Target VPH Analytes and Surrogate

$$Calibration\ Factor\ (CF) = \frac{area\ of\ peak}{concentration\ purged\ (\mu g/L)}$$

9.4.2.6 Hydrocarbon Ranges - Establish retention time windows for the hydrocarbon ranges using the VPH Component marker compounds shown in Table 5.

9.4.2.7 Calculate a CF for the C_5-C_8 aliphatic hydrocarbon range using the following steps.

Sum the **individual FID peak areas** of the three VPH Components that are used to establish an average range CF for C_5-C_8 aliphatic hydrocarbons, as designated in Table 2b. It is important to note that these integrations must be performed using a valley-to-valley approach for each of the individual peaks that comprise this range. The sum of each of these areas is used in the subsequent calculation. Note: Do not include the area of any surrogate standard in calculating a hydrocarbon range CF.

Using this total area, calculate the C_5-C_8 aliphatic hydrocarbon range CF using Equation 2.

Equation 2: Calibration Factor for Hydrocarbon Range

$$Range\ CF = \frac{Area\ summation\ of\ range\ components}{Total\ concentration\ purged\ (\mu g/L)}$$

9.4.2.8 Calculate a CF for the C_9-C_{12} aliphatic hydrocarbon range using the following steps.

Sum the **individual FID peak areas** of the three VPH Components that are used to establish an average range CF for C_9-C_{12} aliphatic hydrocarbons, as designated in Table 2b. Note that erratic performance has been noted for n-nonane; calibration of C_9-C_{12} aliphatic hydrocarbons using only two VPH Components (n-decane and n-butylyclohexane) is allowed. It is important to note that these integrations must be performed using a valley-to-valley approach for each of the individual peaks that comprise this range. The sum of each of these areas is used in the subsequent calculation. Note: Do not include the area of any surrogate standard in calculating a hydrocarbon range CF.

Using this total area, calculate the C_9-C_{12} hydrocarbon range CF using Equation 2.

9.4.2.9 Calculate a CF for the C_9-C_{10} aromatic hydrocarbon range using the following steps.

Use the individual PID peak area of the one VPH component that is used to establish an average range CF for C_9-C_{10} aromatic hydrocarbons, as designated in Table 2b. It is important to note that integration must be performed using a valley-to-valley approach for the one peak that comprises this range. This area is used in the

subsequent calculation. Note: Do not include the area of any surrogate standard in calculating a hydrocarbon range CF. Do not include the area of naphthalene when determining the CF for C_9-C_{10} aromatic hydrocarbons

Using this area, calculate the C_9-C_{10} aromatic range CF using Equation 2.

9.4.2.10 Calculate the average CF for each of the Target VPH Analytes, the surrogate, and each hydrocarbon range.

9.4.2.11 Calculate the percent relative standard deviation (%RSD) of the CFs over the working range of the curve for each of the Target VPH Analytes, the surrogate, and each hydrocarbon range using Equation 3.

Equation 3: Percent Relative Standard Deviation

$$\%RSD = [(SD_{n-1})/(AVG_x)] * 100$$

where:

%RSD = percent relative standard deviation
SD_{n-1} = standard deviation (n-1 degrees of freedom)
AVG_x = average CF from the initial calibration curve

9.4.2.12 If the %RSD is ≤20 for Target VPH Analytes and the surrogate and ≤25 for hydrocarbon ranges, linearity can be assumed and the average CF can be used for quantitation in lieu of a calibration curve.

If, under **extenuating** analytical circumstances (e.g., extending the RL beyond the expected linear range of the detector), the %RSD criteria cannot be achieved, then a linear (least squares) regression may be used to generate a calibration curve consistent with the guidance provided in SW-846 Method 8000D, Section 11.5.2. For the linear regression calculations, the origin (0,0) cannot be included as a calibration point.

NOTE: Use of non-linear calibration is not allowed and is considered a Significant Modification as per Section 11.3.1.

9.4.2.13 In order for the linear regression model to be used for quantitative purposes, r (correlation coefficient) must be ≥0.99. In addition, the resulting calibration curve from the linear regression must be verified by recalculating concentrations of the Target VPH Analytes and hydrocarbon ranges in the lowest calibration standard using the final calibration curve. Recoveries must be 70-130%.

If recalculated concentrations from the lowest calibration standard are outside the 70-130% recovery range, raise the RL to the concentration of the next highest calibration standard that exhibits acceptable recoveries when recalculated using the final calibration curve.

9.4.2.14 For any calibration model, the concentration of the lowest initial calibration standard used in an acceptable initial calibration (i.e., %RSDs and r within method criteria), adjusted for sample size, dilution, etc., establishes the method RL.

9.4.2.15 The initial calibration must be verified through the analysis of an initial calibration verification (ICV). This analysis must be performed every time an initial calibration is performed. The ICV must be prepared from a different stock standard than that used to prepare the calibration standard and must be analyzed immediately following the initial

calibration. The ICV should be prepared at a mid-range calibration curve concentration.

Calculate the percent recovery (%R) of each Target VPH Analyte and hydrocarbon range using Equation 4. Percent recoveries must be between 70-130%. Recalibrate if >10% of all analytes are outside of criteria.

Equation 4: Percent Recovery

$$\%R = [(C_{found})/(C_{true})] * 100$$

where:

%R = Percent Recovery
C_{found} = Concentration of the Target VPH Analyte or hydrocarbon range detected in the ICV (µg/L)
C_{true} = True concentration of the Target VPH Analyte or hydrocarbon range in the ICV (µg/L)

9.4.3 Continuing Calibration

9.4.3.1 A Continuing Calibration Standard must be analyzed daily prior to sample analysis, after every 20 samples, and at the end of the analytical sequence. It should be noted that the Percent Differences (%Ds) are calculated (Equation 5) when CFs are used for the initial calibration and Percent Drifts (Equation 6-4, Appendix 6) are calculated when calibration curves using linear regression are used for the initial calibration.

9.4.3.2 The concentration of the VPH Continuing Calibration Standard must be near the midpoint of the calibration curve.

9.4.3.3 Calculate the CF for each Target VPH Analyte, surrogate, and hydrocarbon range from the Continuing Calibration Standard using Equations 1 and 2.

9.4.3.4 Calculate the %D of the Continuing Calibration Standard CF from the initial calibration average CF using Equation 5.

Equation 5: Percent Difference

$$\%D = [(CFc) - (CF_I)]/[(CF_I)] * 100$$

where:

%D = Percent Difference
CFc = CF from the VPH Continuing Calibration Standard
CF_I = average CF from the initial calibration curve

9.4.3.5 The %D or Percent Drift for each Target VPH Analyte and surrogate must be $\leq$ 20. The %D or Percent Drift for each hydrocarbon range must be $\leq$25. Greater %Ds are permissible for n-nonane. If the %D for n-nonane is > 30, note the nonconformance in the case narrative. If more than one Target VPH Analyte or hydrocarbon range fails to meet the applicable criterion, the instrument must be recalibrated. Otherwise, sample analysis may proceed.

9.4.4 Daily Retention Time Windows

The range retention time windows must be established daily based upon the retention time of the marker compounds in the VPH Continuing Calibration Standard. Use the absolute retention time for

each analyte in the continuing calibration standard as the midpoint of the window for that day. The daily retention time window equals the midpoint ± 3 times the standard deviation determined in Section 9.3. The marker compounds used for each range are defined in Table 5.

9.4.5 Target VPH Analytes, C_9 to C_{10} Aromatic Hydrocarbons, and the surrogate are quantitated on the PID chromatogram

9.4.6 C_5 through C_8 and C_9 through C_{12} Aliphatic Hydrocarbons and the surrogate are quantitated on the FID chromatogram.

9.5 GC Analysis

9.5.1 Samples are analyzed in a group referred to as an analytical batch. The analytical sequence begins with instrument calibration (initial or continuing) followed by up to 20 samples interspersed with blanks and QC samples and closed with a mid-range continuing calibration standard. The analytical sequence ends when one or more analytical batches have been processed or when any required qualitative and/or quantitative QC criteria are exceeded, whichever comes first.

9.5.2 Identification of Target VPH Analytes

- Tentative identification of a Target VPH Analyte occurs when a peak from a sample chromatogram falls within the daily retention time window. Confirmation on a second GC column or by GC/MS analysis may be necessary, if warranted by the project's data quality objectives.
- Co-elution of the p- and m- xylene isomers may occur.
- Validation of GC system qualitative performance must be accomplished by the analysis of mid-level standards within the analysis sequence. If the retention times of the Target VPH Analytes fall outside their daily retention time window in the standards, the system is out of control. In such cases, the cause of the nonconformance must be identified and corrected.

9.5.3 Aliphatic and aromatic hydrocarbon ranges of interest are determined by the collective integration of all peaks that elute between specified range "marker" compounds. Due to the variability in software approaches and applications to collective peak area integration, it is recommended that a manual verification be initially performed to document accurate integration.

9.5.4 **Collective peak area integration for the hydrocarbon ranges must be <u>from baseline</u> (i.e., must include the unresolved complex mixture "hump" areas).** For the integration of individual Target VPH Analytes and surrogate compounds, a valley-to-valley approach should typically be used, though this approach may be modified on a case-by-case basis by an experienced analyst. In any case, the unresolved complex mixture "hump" areas must <u>not</u> be included in the integration of individual Target VPH Analytes and surrogate compounds.

9.5.5 If the response for an individual Target VPH Analyte exceeds the linear range of the system, dilute the sample and reanalyze. The samples must be diluted so that all peaks fall within the linear range of the detector.

9.5.6 For non-target analytes eluting in the aliphatic or aromatic hydrocarbon ranges, the upper linear range of the system should be defined by peak height measurement, based upon the maximum peak height documented for an aliphatic or aromatic standard within the hydrocarbon range that is shown to be within the linear range of the detector.

9.5.7 Under circumstances that sample dilution is required because either the concentration of one or more of the Target VPH Analytes exceed the concentration of their respective highest calibration standard or any non-target peak eluting within any aliphatic or aromatic range exceeds the peak height documented for the highest range-specific calibration standard, the RL for each Target VPH

Analyte and/or hydrocarbon range must be adjusted (increased) in direct proportion to the Dilution Factor (DF).
Where:

$$DF = \frac{\text{Sample Aliquot Volume (mL) + Diluent Volume (mL)}}{\text{Sample Aliquot Volume (mL)}}$$

And the revised RL for the diluted sample, RL_d:

RL_d = DF X Lowest Calibration Standard for Target VPH Analyte

It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy "MCP program" reporting limits in some cases if the RL_d is greater than the applicable MCP standard or criterion to which the concentration is being compared. Such increases in RLs are the unavoidable but acceptable consequence of sample dilution that enable quantification of target analytes which exceed the calibration range. All dilutions must be fully documented in the laboratory narrative.

Analytical Note: Over dilution is an unacceptable laboratory practice. The post-dilution concentration of the highest concentration target analyte must be at least 60 - 80% of its highest calibration standard. This will avoid unnecessarily high RLs for other target analytes, which did not require dilution.

9.6 Calculations

The concentrations of Target VPH Analytes and hydrocarbon ranges in a sample may be determined from the peak area response, using the CFs determined in Section 9.4. If linear regression was used for calibration, refer to Appendix 6 for sample concentration calculations.

9.6.1 Individual Target VPH Analytes and Surrogate: The average CF from the initial calibration is used to calculate the concentration of an analyte or surrogate detected in the sample. Equation 6 is used to calculate the concentration of Target VPH Analytes and the surrogate in µg/L.

Equation 6: Aqueous Samples: Calculation of Sample Concentration (µg/L)

$$Conc\ Analyte\ (\mu g/L) = \frac{(A_x)(DF)}{(CF)}$$

where

Ax = Area count for the Target VPH Analyte or surrogate
DF = Dilution factor (see Section 9.5.7)
CF = Average CF for Target VPH Analyte or surrogate

For soil/sediment samples, convert the µg/L value to µg/kg using Equation 7.

Equation 7: Soil/Sediment Samples: Conversion of µg/L to µg/kg

$$Conc\ Analyte(\mu g/kg) = \frac{(Cx)(V_t)(V_w)}{(V_i)(W_d)}$$

where:

Cx = Concentration from Equation 6 (µg/L)

V_t = Total volume of methanol extract, mL

Analytical Note: This volume must also include the volume of surrogate spiking solution added to soil/sediment samples (if ≥ 100 µL) and the volume of water added due to % moisture correction. See Section 9.6.4.

V_i = Volume of methanol extract added to reagent water for purge-and-trap analysis, µL.
V_w = Volume of reagent water used for purge-and-trap analysis, µL.
W_d = Dry weight of sample, g (see Equations 10 through 12)

The integration of Target VPH Analytes and surrogates must be performed from valley to valley.

9.6.2 Hydrocarbon Ranges

When calculating the VPH by GC/PID/FID method aliphatic and aromatic hydrocarbon range concentrations, the laboratory **must** include the area of **all** peaks eluting within the retention time windows specified for these ranges, excluding surrogates, as described below in Sections 9.6.2.1, 9.6.2.2, and 9.6.2.3.

The average hydrocarbon range CF from the initial calibration is used to calculate the concentration (µg/L) of hydrocarbon ranges in samples**. Collective peak area integration for the hydrocarbon ranges must be from baseline (i.e., must include the unresolved complex mixture).**

9.6.2.1 C_5-C_8 Aliphatic Hydrocarbons: FID

- Sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 5 (using baseline integration).
- From this sum, subtract the area counts of any surrogates which elute in this range (using valley-to-valley integration).
- Calculate a preliminary concentration (Unadjusted C_5-C_8 aliphatic hydrocarbons) in µg/L using Equation 8.

Equation 8: Aqueous Samples: Calculation of Preliminary (Unadjusted) Sample Concentration of C_5-C_8 Aliphatic Hydrocarbons (µg/L)

$$Conc\ HC\ Range(\mu g/L) = \frac{(A_x)(DF)}{(CF)}$$

where:

A_x = total area count of all peaks eluting within hydrocarbon range window (excluding the surrogates)
CF_{avg} = average CF for hydrocarbon range
DF = dilution factor (see Section 9.5.7)

For soil/sediment samples, convert the µg/L value to µg/kg using Equation 9.

Equation 9: Soil/Sediment Samples: Conversion of µg/L to µg/kg

$$Conc\ Analyte(\mu g/kg) = \frac{(Cx)(V_t)(V_w)}{(V_i)(W_d)}$$

where:

Cx = Concentration from Equation 8 (µg/L)
V_t = Total volume of methanol extract, mL

Analytical Note: This volume must also include the volume of surrogate spiking solution added to soil/sediment samples (if ≥ 100 µL) and the volume of water added due to % moisture correction. See Section 9.6.4.

V_i = Volume of methanol extract added to reagent water for purge-and-trap analysis, µL
V_w = Volume of reagent water used for purge-and-trap analysis, µL
W_d = Dry weight of sample, g (see Equations 10 through 12)

NOTE: These values are reported as the "Unadjusted C_5-C_8 aliphatics" as shown in Appendix 3, Exhibit 1.

- From the Unadjusted concentration (µg/L or µg/kg), calculate the concentration of C_5-C_8 aliphatic hydrocarbons by subtracting the concentrations of Target VPH Analytes (which are quantified using the PID) which elute in this range (typically MTBE, benzene, and toluene for the C_5-C_8 aliphatic hydrocarbons). This is the final concentration reported as the "C_5-C_8 Aliphatic Hydrocarbons" on the data report form in Appendix 3, Exhibit 1.

9.6.2.2 C_9-C_{10} Aromatic Hydrocarbons: PID

- Sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 5 (using baseline integration).

- From this sum, subtract the area counts of any surrogates which elute in this range (using valley-to-valley integration).

- Calculate the concentration in µg/L using Equation 8.

For soil/sediment samples, convert the µg/L value to µg/kg using Equation 9.

9.6.2.3 C_9-C_{12} Aliphatic Hydrocarbons: FID

- Sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 5 (using baseline integration).

- From this sum, subtract the area counts of any surrogates which elute in this range (using valley-to-valley integration).

- Calculate a preliminary concentration (Unadjusted C_9-C_{12} aliphatic hydrocarbons) in µg/L using Equation 8.

  For soil/sediment samples, convert the µg/L value to µg/kg using Equation 9.

  NOTE: These values are reported as the "Unadjusted C_9-C_{12} aliphatics" as shown in Appendix 3, Exhibit 1.

- From the Unadjusted concentration (µg/L or µg/kg), calculate the concentration of C_9-C_{12} aliphatic hydrocarbons by subtracting the concentrations of C_9-C_{10} aromatic hydrocarbons (from the PID) and the Target VPH Analytes (which are quantified using the PID) which elute in this range (typically ethylbenzene, m & p-xylenes,

and o-xylene for the C_9-C_{12} aliphatic hydrocarbons). This is the final concentration reported as the "C_9-C_{12} Aliphatic Hydrocarbons" on the data report form in Appendix 3, Exhibit 1.

9.6.3 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample purged (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.4. Using the data obtained from Section 9.1.4, W_d is calculated using Equations 10 through 12.

Equation 10: Percent Moisture

$$\%\ Moisture = \frac{g\ wet\ sample - g\ dry\ sample}{g\ wet\ sample}\ X\ 100$$

Equation 11: Percent Solids

$$\%\ Dry\ Solids\ =\ (100)\ -\ (\%\ Moisture)$$

Equation 12: Dry Weight of Sample

$$W_d\,(g) = (\%\ \text{Dry Solids}/100)(\text{g of extracted sample})$$

9.6.4 Data Correction for Target VPH Analyte and Range Calculations for Methanol Preservation Dilution Effect

Based on the requirements of SW-846 Method 8000D, Section 11.10.5, VPH analytical results for soil/sediment samples must be corrected for the Methanol Preservation Dilution Effect. The potential for under reporting Target VPH Analyte and hydrocarbon range concentrations is more pronounced as the "as-received" % moisture content of the soil/sediment sample increases, if this correction is neglected.

Target VPH Analyte and hydrocarbon range concentrations in soil/sediment samples preserved with methanol are subject to a systematic negative bias if the potential increase of the total solvent volume during the methanol extraction process is not considered. This increase in extraction solvent volume is a direct result of the solubility of the entrained sample moisture (water) in the methanol. The total solvent volume is the additive sum of the volume of methanol and the entrained sample moisture that partitions into the methanol during extraction. The volume of water partitioned is estimated from the % moisture determination (and the assumption that 1 g of water occupies a volume of 1 mL). This is a conservative correction regarding calculated VPH concentrations because some fraction of the sample's % moisture may not partition into the methanol, due to various physiochemical binding forces. The total solvent/water volume (Vt) is calculated as follows:

Equation 13: Calculation of Solvent/Water Volume

$$\text{mL solvent/water (Vt)} = \text{mL of methanol} + ((\%\ \text{moisture}/100) \times \text{g of sample})$$

This "corrected" Vt value should be substituted directly for the Vt value shown in Section 9.6, Equations 7 and 9. It should be noted that the Vt value used in Equations 7 or 9 to calculate VPH concentrations must also include the volume of surrogate spiking solution added to soil/sediment samples (if $\geq$ 100 µl).

10.0 QUALITY CONTROL

10.1 General Requirements and Recommendations

10.1.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an Initial Demonstration of Laboratory Capability (IDLC) and an ongoing analysis of prepared QC samples to evaluate and document the quality of data. The laboratory must maintain records to document the quality of the data produced. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method.

10.1.2 At a minimum, for each analytical batch (up to 20 samples of similar matrix), a beginning Initial Calibration or Opening mid-range Continuing Calibration Standard, Closing mid-range Continuing Calibration Standard, LMB, LCS and LCSD must be analyzed. The Initial Calibration or Continuing Calibration Standard, LMB, and LCS must be analyzed prior to samples. Matrix duplicates, matrix spike and/or matrix spike duplicates should be analyzed, at the request of the data user, based upon the nature of the sample. For analytical batches with more than 10 samples, the analysis of an additional mid-range Continuing Calibration Standard should also be considered. However, it should be noted that the analysis of the Continuing Calibration Standard is required prior to sample analysis, after every 20 samples, and at the end of an analytical sequence, at a minimum.

10.1.3 The recommended sequence of analysis is as follows:

(1) Analytical Batch Calibration Standards (initial) or mid-range Continuing Calibration Standard (daily check of initial calibration). **[REQUIRED]**

(2) Initial Calibration Verification. **[REQUIRED only after initial calibration]**

(3) Analytical batch LCS. **[REQUIRED]**

(4) Analytical batch LCSD. **[REQUIRED; can instead be analyzed at end of sequence]**

(5) Analytical batch LMB. **[REQUIRED]**

(6) Batch samples. (up to 20 samples).

(7) Matrix duplicate. **[As requested by data user]**

(8) Matrix Spike/Matrix Spike Duplicate. **[As requested by data user]**

(9) Optional mid-range Continuing Calibration Standard. (consider after 10 samples)

(10) Analytical Batch LCS Duplicate. [a] **[REQUIRED]**

(11) Closing mid-range Continuing Calibration Standard [b] after 20 samples and at end of analytical batch. **[REQUIRED]**

[a] May be used as the analytical batch LCS for the next analytical batch if batches are processed continuously.

[b] May be used as analytical batch opening Continuing Calibration Standard for the next analytical batch if batches are processed continuously.

All analytical sequences and data must be recorded in a daily run log.

10.2 Minimum Instrument QC

10.2.1 The n-pentane (C_5) and MTBE peaks must be adequately resolved from any solvent front that may be present on the FID and PID chromatograms, respectively. This is achievable using the recommended chromatographic column and purge-and-trap procedures. Coelution of the m- and p-

xylene isomers is permissible. All surrogates must be adequately resolved from individual Target VPH Analytes included in the VPH Component Standard. For the purposes of this method, adequate resolution is assumed to be achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks.

10.2.2 **Initial Calibration Verification** – An ICV standard, prepared from a separate source standard than used for initial and continuing calibrations must be analyzed immediately following the initial calibration. The recoveries of all Target VPH Analytes and hydrocarbon ranges must be between 70-130%. A new five-point calibration must be performed if >10% of all analytes are outside of criteria.

10.2.3 **Laboratory Method Blank** – A water or soil LMB is prepared by fortifying a reagent water blank (for aqueous samples), or 25 ml of methanol (for soil/sediment samples) with the surrogate spiking solution (using same volume of surrogate as samples). Peaks must not be detected above the RL within the retention time window of any analyte of interest. The hydrocarbon ranges must not be detected at a concentration greater than 10% of the most stringent applicable MCP cleanup standard for soil/sediment samples and 50% of the most stringent applicable MCP cleanup standard for aqueous samples.

10.2.4 **Relative Retention Times** must be established for each Target VPH Analyte and hydrocarbon range of interest each time a new GC column is installed and must be verified and/or adjusted on a daily basis. (See Sections 9.3 and 9.4.4).

10.2.5 **Calibration**

10.2.5.1 **Initial Calibration:** CFs must be calculated for each Target VPH Analyte and hydrocarbon range based upon the analysis of a minimum of 5 calibration standards. The linearity of CFs may be assumed if the %RSD over the working range of the calibration curve is ≤20 for Target VPH Analytes and the surrogate and ≤25 for hydrocarbon ranges. (See Section 9.4). For linear regression, r must be ≥ 0.99.

10.2.5.2 **Continuing Calibration Standard:** The Continuing Calibration Standard must be analyzed daily prior to sample analysis, every 20 samples, and at the end of an analytical sequence to verify the accuracy of the calibration of the instrument. For Target VPH Analytes and the surrogate, the %D or Percent Drift must be ≤20. For hydrocarbon ranges, the %D or Percent Drift must be ≤ 25. Greater %Ds or Percent Drifts are permissible for n-nonane (if included in the calibration of the $C_9 - C_{12}$ aliphatic range). If the %D or Percent Drift is > 30 for n-nonane, note the nonconformance in the laboratory narrative. If more than one Target VPH Analyte or hydrocarbon range fails to meet this criterion, the instrument must be recalibrated. Otherwise, sample analysis may proceed.

10.2.6 **Laboratory Control Sample** – An LCS is prepared by fortifying a reagent water blank (for aqueous samples) or 25 mL of methanol (for soil/sediment samples) with the matrix spiking solution for a final concentration of 50 µg/L (2.5 mg/kg). The spike recoveries for the Target VPH Analytes and the hydrocarbon ranges must be between 70% and 130%.

- If the recoveries are low and outside of the acceptance limits, reanalyze the LCS and associated samples. If still outside of the acceptance limits, recalibrate.

- If the recoveries are high and outside of the acceptance limits and the affected compound was detected in the associated samples, reanalyze the LCS and the associated samples. If recoveries are still outside of the acceptance limits, recalibrate.

- If the recoveries are high and sample results were nondetect, data can be reported without qualification; however, the high recoveries should be noted in the laboratory narrative.

10.2.7 **LCS Duplicate** – The LCSD is prepared separately from the LCS but prepared and analyzed in the same manner as the LCS and is used as the data quality indicator of precision. The analytical batch precision is determined from the RPD of the concentrations (not recoveries) of the LCS/LCSD pair. The RPD for Target VPH Analytes and aliphatic and aromatic hydrocarbon range concentrations must be $\leq$ 25. See Section 10.2.6 for corrective actions associated with recoveries outside of acceptance limits.

10.2.8 **Surrogate Spike Recoveries**

10.2.8.1 Each sample, LMB, LCS, LCSD, matrix spike, and matrix duplicate must be fortified with the surrogate spiking solution. Required surrogate recovery is 70% to 130% from each detector. At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 70% or more than 130%, check calculations to locate possible errors, check the fortifying solution for degradation, and check for changes in instrument performance. If the cause cannot be determined, reanalyze the sample unless one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture);

(2) Percent moisture of associated soil/sediment sample is > 25% and surrogate recovery is > 10%; or

(3) The surrogate exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in sample.

If a sample with a surrogate recovery outside of the acceptable range is not reanalyzed based on any of these aforementioned exceptions, this information must be noted on the data report form and discussed in the laboratory narrative.

Analysis of the sample on dilution may diminish matrix-related surrogate recovery problems. This approach can be used as long as the RL for the applicable MCP standards will still be achieved with the dilution. If not, reanalysis without dilution must be performed unless the concentrations of target analytes do not allow an undiluted run. Recoveries of surrogates outside of the acceptable range after reanalysis must also be noted on the data report form and discussed in the laboratory narrative.

10.3 At the request of the data user, and in consideration of sample matrices and data quality objectives, matrix spikes and matrix duplicates may be analyzed with every batch of 20 samples or less per matrix.

10.3.1 **Matrix Duplicate** – Matrix duplicates are prepared by analyzing one sample in duplicate. The purpose of the matrix duplicates is to determine the homogeneity of the sample matrix as well as analytical precision. The RPD of detected results in the matrix duplicate samples must not exceed 50 when the results are greater than 5x the RL. Refer to Equation 14 for the RPD calculation. If the RPD exceeds 50 and both results are > 5x the RL, the sample analysis must be repeated.

- If an analyte is detected in one analysis at > 5x the RL and not detected in the duplicate analysis, the analysis must be repeated.
- If an analyte is detected in one analysis at $\leq$ 5x the RL and not detected in the duplicate analysis, the RPD is not calculable and the analysis does not have to be repeated.
- If an analyte is not detected in both the original and duplicate analyses, the RPD is not calculable. No further action is required.

Equation 14. Relative Percent Difference Calculation

$$RPD = [(C_s - C_d) / [(C_s + C_d) / 2]] * 100$$

where:

C_s = concentration in original sample analysis
C_d = concentration in duplicate sample analysis

10.3.2 **Matrix Spike/Matrix Spike Duplicate** – The aqueous or soil/sediment matrix spike is prepared by fortifying an actual aqueous sample or soil/sediment sample with a specified volume (5-10 µl for aqueous samples and not to exceed 1.0 ml for soil/sediment samples) of the matrix spiking solution (see Section 7.6). The desired spiking level is 50% of the highest calibration standard. However, the total concentration in the matrix spike (including the matrix spike and native concentration in the unspiked sample) should not exceed 75% of the highest calibration standard in order for a proper evaluation to be performed. The purpose of the matrix spike is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate unspiked aliquot and the measured values in the matrix spike corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 70-130% of the true value.

10.4 If any of the performance standards specified in Section 10.2 are not met, the cause of the non-conformance must be identified and corrected before any additional samples may be analyzed. Any samples run between the last QC samples that met the criteria and those that are fallen out must be reanalyzed, as noted in Section 10.2. These QC samples include the Continuing Calibration Standard, LMB, LCS, and LCSD. If this is not possible, the data must be reported as suspect.

10.5 Initial and Periodic Method Demonstration of Laboratory Capability (IDLC)

The QC procedures described in Appendix 7 and described in SW-846 Method 8000D, Section 9.3 must be conducted, successfully completed, and documented as an initial demonstration of laboratory capability, prior to the analysis of any samples by the VPH by GC/PID/FID Method. 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, training new analysts and/or in response to confirmed or suspected systems, method, or operational problems. Elements of the IDLC include:

- Demonstration of Acceptable System Background, see Appendix 7, Section 2.0 (Optional);
- Initial Demonstration of Accuracy, see Appendix 7, Section 3.0;
- Initial Demonstration of Precision, see Appendix 7, Section 4.0; and
- Method Detection Limit (MDL), see Appendix 7, Section 5.0 (Optional).

11.0 DATA PRODUCTION AND REPORTING

11.1 Calibration

Using the external calibration procedure (See Section 9.4.2) calibrate the GC/PID/FID as follows:

11.1.1 Using the PID chromatogram, calculate an average CF or linear regression calibration curve for the Target VPH Analytes (benzene, toluene, ethylbenzene, m,p,o-xylenes, naphthalene, and MTBE). This step is not necessary if these Target VPH Analytes will not be individually identified and quantitated by the VPH method (i.e., if unadjusted values only will be reported for the hydrocarbon ranges or if reporting concentrations of Target VPH Analytes via another method).

11.1.2 Using both the FID and PID chromatograms, calculate an average CF for the surrogate 2,5-dibromotoluene.

11.1.3 Using the FID chromatogram, calculate an average collective CF for the total concentration of the C_5-C_8 Aliphatic Hydrocarbons. Tabulate the collective peak area response of the 3 components (n-pentane, 2-methylpentane, 2,2,4-trimethylpentane) against the collective concentration injected.

11.1.4 Using the FID chromatogram, calculate an average collective CF for the total concentration of C_9-C_{12} Aliphatic Hydrocarbons. Tabulate the collective peak area response of the 2 components (n-decane and n-butylcyclohexane) against the collective concentration injected. Alternatively, the CF for C_9-C_{12} Aliphatic Hydrocarbons can be calculated using the collective area response of 3 components (n-nonane, n-decane and n-butylcyclohexane).

11.1.5 Using the PID chromatogram, calculate an average collective CF for the total concentration of C_9-C_{10} Aromatic Hydrocarbons. This value is the value for 1,2,4-trimethylbenzene, the only aromatic standard within this range.

11.2 Sample Analysis

11.2.1 PID Chromatogram

11.2.1.1 If desired, determine the peak area counts for the Target VPH Analytes (using valley-to-valley integration).

11.2.1.2 Determine the peak area count for the surrogate 2,5-dibromotoluene (using valley-to-valley integration).

11.2.1.3 Determine the total area count for all peaks eluting 0.1 minutes after the Rt for o-xylene and 0.1 minutes before the Rt for naphthalene (using baseline integration).

11.2.1.4 Using the equations contained in Section 9.6, calculate the concentrations of the surrogate standard 2,5-dibromotoluene and C_9 through C_{10} Aromatic Hydrocarbons. Optionally, calculate the concentrations of the individual Target VPH Analytes.

11.2.2 FID Chromatogram

11.2.2.1 Determine the total area count for all peaks eluting 0.1 minutes before the Rt for n-pentane and 0.01 minutes before the Rt for n-nonane (using baseline integration). It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.2.2 Determine the total area count for all peaks eluting 0.01 minutes before the Rt for n-nonane and 0.1 before the Rt for naphthalene (using baseline integration). It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.2.3 Determine the peak area count for the surrogate standard 2,5-dibromotoluene (using valley-to-valley integration).

11.2.2.4 Using the equations contained in Section 9.6, calculate the concentrations of C_5 through C_8 Aliphatic Hydrocarbons, C_9 through C_{12} Aliphatic Hydrocarbons, and the surrogate standard 2,5-dibromotoluene.

11.2.3 Data Adjustments

11.2.3.1 By definition, the collective concentrations of aliphatic and aromatic fractions of interest **exclude** the individual concentrations of Target VPH Analytes. Accordingly, a series of data adjustment steps are necessary to adjust the collective hydrocarbon range concentrations calculated in Section 11.2.2.4, to eliminate "double counting" of analytes.

11.2.3.2 The necessary data adjustment steps may be taken by the laboratory reporting the range concentration data, or by the data user. The extent of data adjustments taken by the laboratory must be noted on the data report form.

11.2.3.2.1 Subtract the area counts of the surrogate compound(s) from the collective area count of any range in which they elute. If the recommended surrogate 2,5-dibromotoluene is used, no correction is necessary, as this compound elutes after all ranges of interest.

11.2.3.2.2 Subtract the collective concentration of C_9-C_{10} Aromatic Hydrocarbons from the collective concentration of C_9-C_{12} Aliphatic Hydrocarbons. Do not subtract the C_9-C_{10} Aromatic Hydrocarbon concentration if this concentration is less than the RL. If the resulting C_9–C_{12} Aliphatic Hydrocarbon value is less than the RL, report "< RL" or "RL U", with a specific value replacing "RL" (e.g., "< 10" or "10 U").

11.2.3.2.3 Subtract the individual concentrations of the Target VPH Analytes from the appropriate aliphatic range (i.e., C_5-C_8 or C_9-C_{12} Aliphatic Hydrocarbons) in which they elute. Do not subtract any Target VPH Analyte concentration if this concentration is less than the RL (lowest calibration standard). If the individual concentrations of Target VPH Analytes have been quantitated using another method (e.g., by using an MS detector), note this on the data report form. If the individual concentrations of Target VPH Analytes have not been quantitated, report the values as Unadjusted C_5-C_8 Aliphatic Hydrocarbons and Unadjusted C_9-C_{12} Aliphatic Hydrocarbons, and indicate "Not Determined" for C_5-C_8 Aliphatic Hydrocarbons and C_9-C_{12} Aliphatic Hydrocarbons.

11.2.3.3 For purposes of compliance with the reporting and cleanup standards specified in the MCP, the concentration of Unadjusted C_5-C_8 Aliphatic Hydrocarbons and Unadjusted C_9-C_{12} Aliphatic Hydrocarbons may be conservatively deemed to be equivalent to the concentration of C_5-C_8 Aliphatic Hydrocarbons and C_9-C_{12} Aliphatic Hydrocarbons.

11.3 Data Reporting Content

The required content for VPH Method by GC/PID/FID data is presented in Appendix 3. This information provides data users with a succinct and complete summary of pertinent information and data, as well as a clear affirmation that the QC procedures and standards specified in this method were evaluated and achieved. Any significant modification to the MassDEP VPH by GC/PID/FID Method, as described in Section 11.3.1, and indicated by a negative response to Question E on the MassDEP Analytical Protocol Certification Form (also included in Appendix 3) precludes the affected data from achieving "Presumptive Certainty" status. If a significant modification to the VPH by GC/PID/FID Method is utilized, an attachment to the analytical report must be included to demonstrate compliance with the method performance requirements of Section 1.13 on a matrix- and petroleum product-specific basis.

While it is permissible to modify the reporting format, all of the data and information specified in Appendix 3 for these reports must be provided in a clear, concise, and succinct manner.

11.3.1 "Significant Modifications" to this method are defined as any deviations from "required," "shall," or "must" provisions of this document, or any change or modification that will or could substantively change the accuracy or precision of analytical results. Such modifications include, but are not limited to, any of the following:

11.3.1.1 The use of alternative detectors other than GC/PID/FID to quantitate hydrocarbon range concentrations;
11.3.1.2 The use of other than a purge-and-trap sample preparation procedure;
11.3.1.3 The use of a heated purge;

11.3.1.4 The use of non-linear repression (i.e., quadratic equations) for the calculation of Target VPH Analytes and/or hydrocarbon ranges; or

11.3.1.5 Failure to provide all of the data and information presented in Appendix 3 as well as the required method deliverables discussed in Section 11.3.3.

11.3.2 Positive affirmation that all required QC procedures and performance standards were followed and achieved means that all of the required steps and procedures detailed in Sections 9.0 and 10.0 have been followed, and that all data obtained from these steps and procedures were within the acceptance limits specified for these steps and procedures.

11.3.3 In addition to sample results, the VPH data report must contain the following items:

- LMB Results
- LCS Results
- LCSD Results
- Matrix spike and/or matrix spike duplicate results (only if requested by data user)
- Matrix duplicate results (only if requested by data user)
- Surrogate spike recoveries (for all field samples and QC samples from each detector)
- Summary of column used (manufacturer, column name, length, ID, film thickness)
- Summary of trap used (manufacturer, trap contents)
- Results of reanalyses or dilutions, reported as follows:

    1. If reanalysis due to surrogate issues yields similar non-conformances, the laboratory must report results of both analyses.
    2. If reanalysis due to surrogate issues is performed outside of holding time and yields acceptable surrogate recoveries, the laboratory must report results of both analyses.
    3. If sample is not reanalyzed for surrogate issues due to obvious interference, the laboratory must provide the chromatogram in the data report.
    4. If diluted and undiluted analyses are performed, the laboratory must report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., LMBs, LCS, etc.) for each analysis must be reported. This may result in more than one analysis per sample being reported.

11.3.4 General laboratory reporting requirements are outlined in WSC-CAM-VII A, *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data*. A copy of the required MassDEP MCP Analytical Protocol Certification Form is included in Appendix 3 of this method.

12.0 REPORTING LIMITS

The RLs for Target VPH Analytes shall be based upon the concentration of the lowest calibration standard for the analyte of interest. The RL must be greater than or equal to the concentration of the lowest calibration standard.

The RLs for hydrocarbon ranges shall be based upon the concentration of the lowest calibration standard for an individual analyte within the range of interest. The RL will be set at 100x the concentration of the lowest calibration standard for the associated analyte.

Based on a concentration of 1 µg/L for the lowest calibration standard for all analytes, the following RLs would be generated for the hydrocarbon ranges:

Aqueous Samples: Hydrocarbon range RLs would be equivalent to 100 µg/L.

Soil/Sediment Samples: Hydrocarbon range RLs would be equivalent to 5 mg/kg based on a 1:1 ratio of methanol: soil and analysis of a 100 µL aliquot of the methanol extract in 5 mL water.

13.0 METHOD PERFORMANCE

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-2 in Appendix 1. Chromatograms are provided in Appendix 2. For an evaluation of method performance, refer to *Evaluation of MassDEP Volatile Petroleum Hydrocarbon (VPH) Methods*, Massachusetts Department of Environmental Protection, June 2016.

14.0 REFERENCES

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3. ASTM Method D2216-92, *Determination of Moisture Content of Soils and Sediments.*

4. Fitzgerald, John *Onsite Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure* in Petroleum Contaminated Soils, Vol. 2, 1989.

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9. MassDEP, 2002: *Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach*, Massachusetts Department of Environmental Protection, WSC Policy # 02-411, October 31, 2002.

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16. USEPA UST Workgroup, Draft *Method for Determination of Gasoline Range Organics*, November, 1990.

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19. USEPA: SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition; Methods 5030B, 5035A, 8000D, 8015C, and 8021B.

20. Wisconsin DNR, *Modified GRO Method for Determining Gasoline Range Organics*, PUBL-SW-140, 1992.

TABLES

Table 1. Volatile Petroleum Hydrocarbon (VPH) Component Standard

Compound	Retention Time (minutes)[1]	
	PID	FID
n-Pentane	N/A	5.11
2-Methylpentane	N/A	6.68
Methyl-tert-butylether	7.26	7.26
2,2,4-Trimethylpentane	N/A	11.25
Benzene	12.24	12.24
Toluene	18.06	18.06
n-Nonane	N/A	22.59
n-Decane	N/A	26.98
Ethylbenzene	23.12	23.12
m- & p- Xylene	23.37	23.37
o-Xylene	24.78	24.78
1,2,4-Trimethylbenzene	28.34	28.34
n-Butylcyclohexane	N/A	28.52
Naphthalene	32.03	N/A
2,5-Dibromotoluene (surrogate)	33.78	33.78

[1] Results obtained using an RTX-502.2 column and chromatographic conditions described in Appendix 2

Table 2a. Recommended VPH Calibration Standard Concentrations

Component	Nominal Concentration (µg/L)				
Pentane	1	5	25	100	200
2-Methylpentane	1	5	25	100	200
Methyl-t-butyl ether	1	5	25	100	200
2,2,4-Trimethylpentane	1	5	25	100	200
Benzene	1	5	25	100	200
Toluene	1	5	25	100	200
n-Nonane[1]	1	5	25	100	200
n-Decane	1	5	25	100	200
Ethylbenzene	1	5	25	100	200
m-Xylene	1	5	25	100	200
p-Xylene	1	5	25	100	200
o-Xylene	1	5	25	100	200
1,2,4-Trimethylbenzene	1	5	25	100	200
n-Butylcyclohexane	1	5	25	100	200
Naphthalene	1	5	25	100	200
2,5-Dibromotoluene (surrogate)	1	5	25	100	200

[1] Erratic performance has been noted for n-nonane; calibration of C_9-C_{12} aliphatics with n-decane and n-butylcyclohexane only is allowed. However, n-nonane must be retained in the calibration standard for use as a range marker compound (see Table 5).

Table 2b. Initial Calibration of VPH Hydrocarbon Range Components

Hydrocarbon Range	Hydrocarbon Range Compounds Used to Establish Range Calibration Factor	Calib. Level	Component Standard Calibration Concentration	
			Individual Range Component Concentration (µg/L)	Hydrocarbon Range Total Concentration (µg/L)
C_5-C_8 Aliphatic	n-Pentane 2-Methylpentane 2,2,4-Trimethylpentane	1	1	3
		2	5	15
		3	25	75
		4	100	300
		5	200	600
C_9-C_{12} Aliphatic	n-Nonane[1] n-Decane n-Butylcyclohexane	1	1	3
		2	5	15
		3	25	75
		4	100	300
		5	200	600
C_9-C_{10} Aromatic	1,2,4-Trimethylbenzene	1	1	1
		2	5	5
		3	25	25
		4	100	100
		5	200	200

[1] Erratic performance has been noted for n-nonane; calibration of C_9-C_{12} aliphatics with n-decane and n-butylcyclohexane only is allowed. However, n-nonane must be retained in the calibration standard for use as a range marker compound (see Table 5). Hydrocarbon range total concentrations provided above assume n-nonane is included in the calibration of this range.

Table 3. Holding Times and Preservatives for VPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples (using ambient temperature purge)	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl to pH <2; cool to 0-6°C	14 days
Aqueous Samples (using heated purge)[1]	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 0.40 to 0.44 grams of trisodium phosphate dodecahydrate to pH >11; cool to 0-6°C	14 days
Soil/Sediment Samples[2]	VOC vials w/ Teflon-lined septa screw caps. 60-mL vials: add 25 g soil/sediment 40-mL vials: add 15 g soil/sediment	1 mL methanol for every g soil/sediment; add before or at time of sampling; cool to 0-6°C	28 days
[1] Heated purge is considered a significant modification to the method, as per Section 11.3.1. **[2] Refer to Appendix 4 for details on sample collection or optional collection/storage devices.**			

Table 4. Recommended Purge-and-Trap Operating Parameters

Purge gas	Helium
Purge gas flow rate (mL/min)	40
Purge time (min)	11.0 ± 0.1
Purge temperature	Ambient*
Desorb temperature °C	260
Desorb time (min)	4.0
Backflush inert gas flow during desorb (mL/min)	15-20
Bake temperature (°C)	260
Bake time (min)	7-15
* If heated purge temperature is used, different preservation procedures apply; see Table 3. Heated purge is considered a significant modification to the method, as per Section 11.3.1.	

Table 5. VPH Marker Compounds and Range Retention Time Windows

Hydrocarbon Range	Beginning Marker	Ending Marker
C_5-C_8 Aliphatic Hydrocarbons (FID)	0.1 min before n-Pentane	0.01 min before n-Nonane
C_9-C_{12} Aliphatic Hydrocarbons (FID)	0.01 min before n-Nonane	0.1 min before Naphthalene[1]
C_9-C_{10} Aromatic Hydrocarbons (PID)	0.1 min after o-xylene	0.1 min before Naphthalene

[1] The retention time for Dodecane (C_{12}) is approximately 2 minutes less than the retention time for naphthalene, using the column and chromatographic conditions recommended for this method. For simplicity, naphthalene is used as the ending marker for the C_9-C_{12} Aliphatic Hydrocarbon range.

APPENDIX 1

SINGLE LABORATORY ACCURACY, PRECISION, AND

METHOD DETECTION LIMITS (MDL) DATA

Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into Reagent Water and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/L)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	6.0		91		6.3		1.1
2-Methylpentane	8.0		100		8.6		2.2
Methyl-tert-butylether	3.0	95		5.2		0.47	
2,2,4-Trimethylpentane	4.0		98		11.9		1.5
Benzene	1.0	91		7.5		0.21	
Toluene	3.0	93		6.2		0.55	
n-Nonane	2.0		98		7.2		0.44
Ethylbenzene	1.0	92		5.6		0.16	
m- & p-Xylene	4.0	95		5.2		0.62	
o-Xylene	2.0	86		14.8		0.81	
1,2,4-Trimethylbenzene	2.0	89		6.1		0.34	
Naphthalene	4.0	113		11.1		1.57	
2,5-Dibromotoluene (surrogate)	40	90	90	10.9	13.3		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into VPH-Free Sand and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/g)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/g)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	2		96		4.7		0.28
2-Methylpentane	3		99		5.1		0.47
Methyl-tert-butylether	3	89		4.7		0.39	
2,2,4-Trimethylpentane	3		110		2.1		0.22
Benzene	1	100		4.5		0.14	
Toluene	3	104		4.3		0.42	
n-Nonane	2		108		3.6		0.25
Ethylbenzene	1	103		5.0		0.16	
m- & p-Xylene	4	101		4.0		0.51	
o-Xylene	2	106		4.3		0.28	
1,2,4-Trimethylbenzene	2	103		3.8		0.25	
Naphthalene	2	86		2.8		0.15	
2,5-Dibromotoluene (surrogate)	2	95		11.4		0.68	

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

APPENDIX 2

VPH BY GC/PID/FID METHOD CHROMATOGRAMS

Gas Chromatograms of the VPH Component Standard

Restek RTX-502.2 capillary column (105 m x 0.53 mm i.d., 3-µm film thickness); PID (10.2 eV) in series with FID; GC operating conditions: 45°C for 2 min/ 3°C/min to 90°C for 0 min/ 5°C/min to 140°C for 0 min/ 45°C/min to 230°C for 6.5 min.

Figure 1. FID Chromatogram

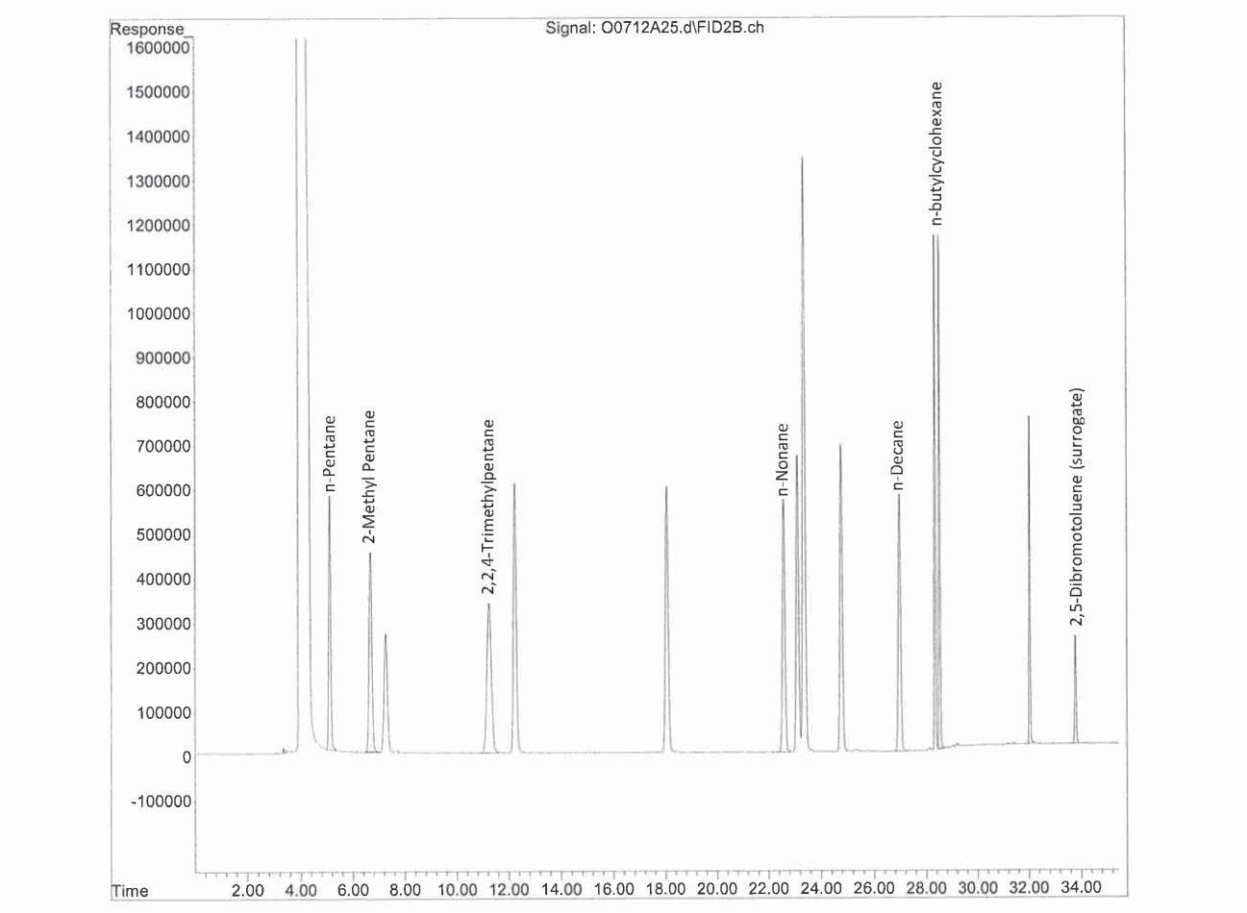
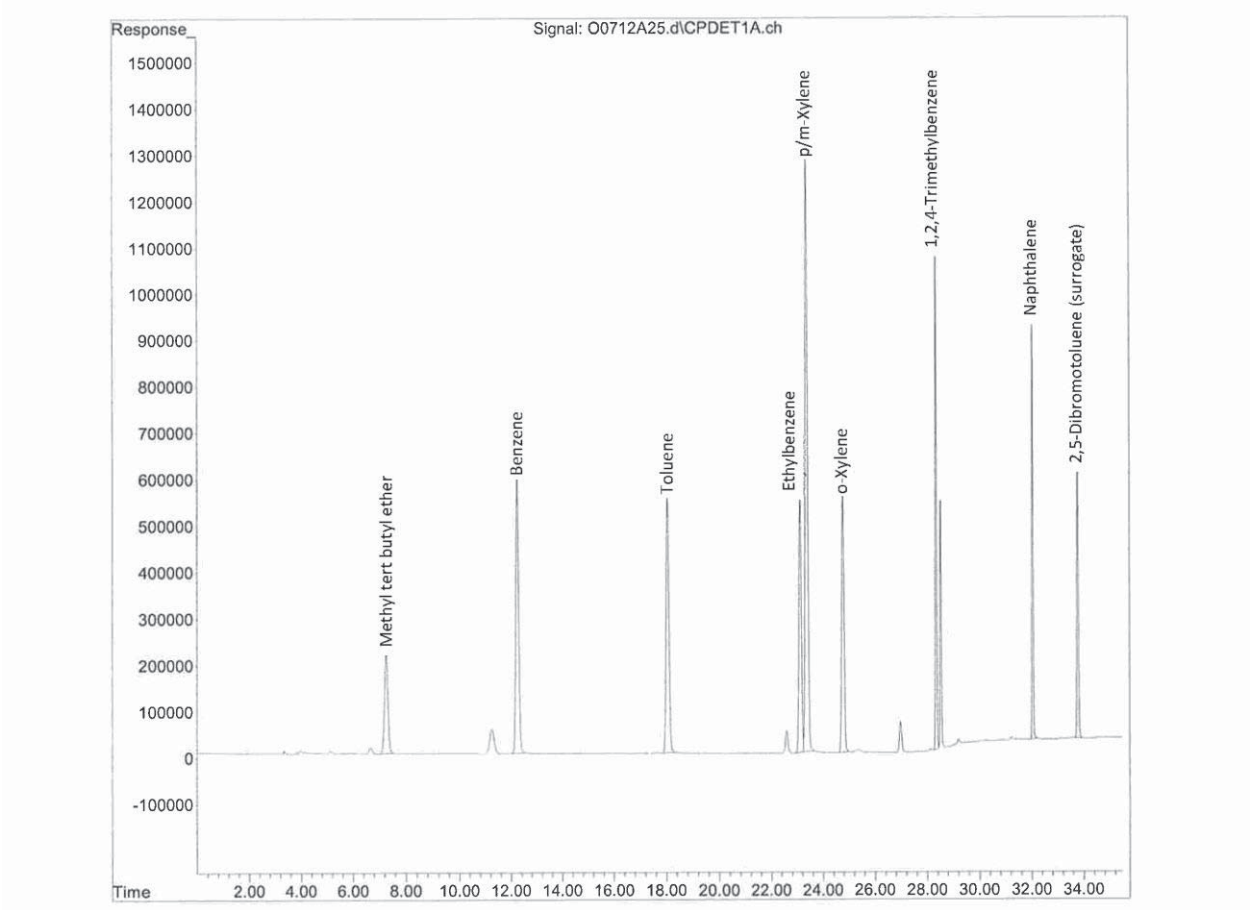


Figure 2. PID Chromatogram



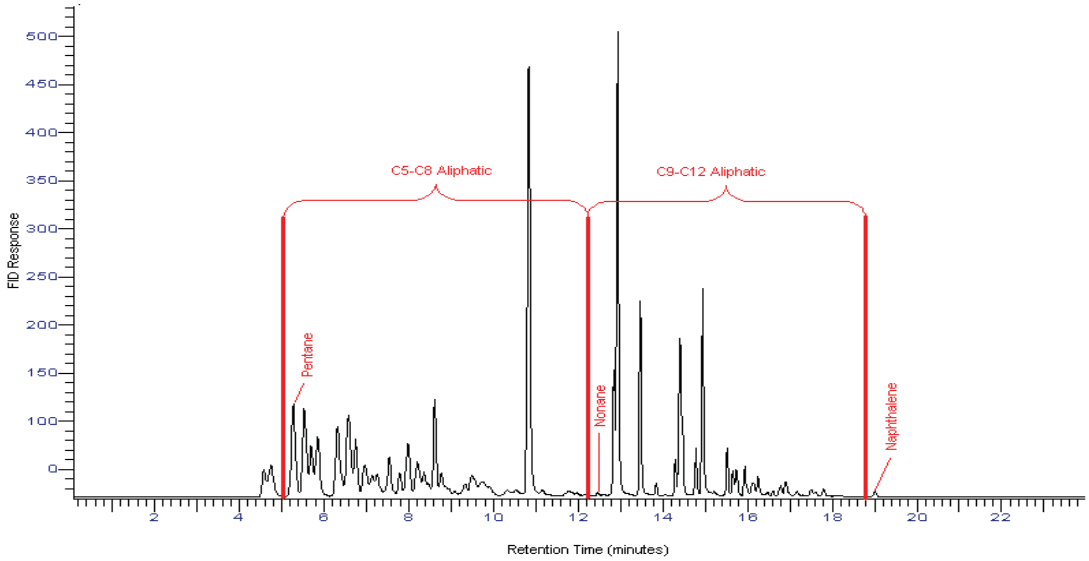


Figure 3 Gas Chromatogram (FID) of the VPH Gasoline Standard

Restek RTX-502.2 capillary column (105-m x 0.53-mm i.d., 3-μm film thickness); PID detector (10.2-eV lamp) in series with an FID detector (O.I. Analytical); Tekmar (model 3000) purge-and-trap concentrator.

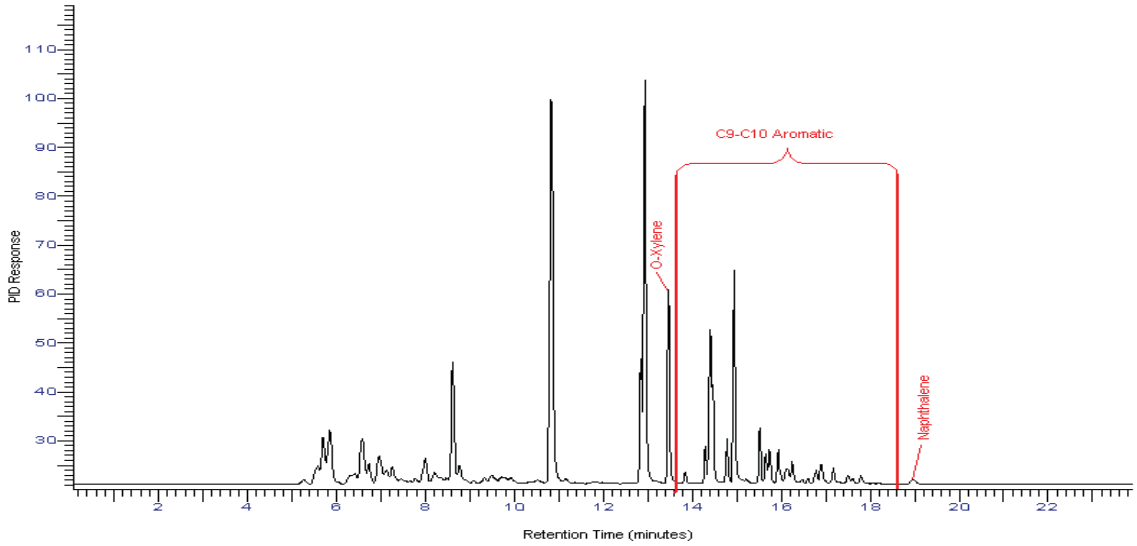


Figure 4. Gas Chromatogram (PID) of the VPH Gasoline Standard

Restek RTX-502.2 capillary column (105-m x 0.53-mm i.d., 3-μm film thickness); PID detector (10.2-eV lamp) in series with an FID detector (O.I. Analytical); Tekmar (model 3000) purge-and-trap concentrator.

APPENDIX 3
REQUIRED VPH DATA REPORT INFORMATION

Exhibit 1 Required VPH Data Report Information

Exhibit 2 MassDEP Analytical Protocol Certification Form

APPENDIX 3
Exhibit 1: Required VPH Data Report Information

SAMPLE INFORMATION

Matrix	☐ Aqueous ☐ Soil ☐ Sediment ☐ Other:		
Containers	☐ Satisfactory ☐ Broken ☐ Leaking:		
Sample Preservatives	**Aqueous (acid-preserved)**	☐ N/A ☐ pH ≤ 2 ☐ pH > 2 Comment:	
	Aqueous (TSP-preserved)	☐ N/A ☐ pH ≤ 11 ☐ pH > 11 Comment:	
	Soil or Sediment	☐ N/A ☐ Samples NOT preserved in Methanol or air-tight container	mL Methanol/g soil/sediment
		☐ Samples rec'd in Methanol: ☐ covering soil/sediment ☐ not covering soil/sediment	☐ 1:1 +/- 25%
		☐ Samples received in air-tight container:	☐ Other:
Temperature	☐ Received on Ice ☐ Received at 0-6ºC ☐ Other: _____ºC		

VPH ANALYTICAL RESULTS

Method for Ranges: ☐VPH by GC PID/FID ☐VPH by GC/MS			**Client ID**				
Method for Target Analytes: ☐VPH by GC PID/FID ☐VPH by GC/MS ☐VOCs by 8260			**Lab ID**				
Trap & Analytical Column			**Date Collected**				
			Date Received				
			Date Preserved[4]				
VPH Surrogate Standards			**Date Analyzed**				
			Dilution Factor				
			% Moisture (soil/sediment)				
Range/Target Analyte	**Elution Range**	**RL**	**Units**				
Unadjusted C5-C8 Aliphatics[1]	**N/A**						
Unadjusted C9-C12 Aliphatics[1]	**N/A**						
Benzene							
Ethylbenzene							
Methyl-tert-butylether							
Naphthalene	**N/A**						
Toluene							
m- & p- Xylenes							
o-Xylene							
C5-C8 Aliphatic Hydrocarbons[1,2]	**N/A**						
C9-C12 Aliphatic Hydrocarbons[1,3]	**N/A**						
C9-C10 Aromatic Hydrocarbons[1]	**N/A**						
Surrogate % Recovery							
Surrogate Acceptance Range				**70-130%**	**70-130%**	**70-130%**	**70-130%**

[1]Hydrocarbon range data exclude area counts of any surrogate(s) and/or internal standards eluting in that range.
[2]C_5-C_8 Aliphatic Hydrocarbons exclude the concentration of Target VPH Analytes eluting in that range.
[3]C_9-C_{12} Aliphatic Hydrocarbons exclude concentration of Target VPH Analytes eluting in that range AND concentration of C_9-C_{10} Aromatic Hydrocarbons.
[4]Only applies to soil samples collected in air-tight containers.

APPENDIX 3
Exhibit 2: MassDEP Analytical Protocol Certification Form

MassDEP Analytical Protocol Certification Form					
Laboratory Name:			Project #:		
Project Location:			RTN:		
This Form provides certifications for the following data set: list Laboratory Sample ID Number(s):					
Matrices: ☐ Groundwater/Surface Water ☐ Soil/Sediment ☐ Drinking Water ☐ Air ☐ Other:					
CAM Protocol (check all that apply below):					
8260 VOC CAM II A ☐	7470/7471 Hg CAM III B ☐	MassDEP VPH (GC/PID/FID) CAM IV A ☐	8082 PCB CAM V A ☐	9014 Total Cyanide/PAC CAM VI A ☐	6860 Perchlorate CAM VIII B ☐
8270 SVOC CAM II B ☐	7010 Metals CAM III C ☐	MassDEP VPH (GC/MS) CAM IV C ☐	8081 Pesticides CAM V B ☐	7196 Hex Cr CAM VI B ☐	MassDEP APH CAM IX A ☐
6010 Metals CAM III A ☐	6020 Metals CAM III D ☐	MassDEP EPH CAM IV B ☐	8151 Herbicides CAM V C ☐	8330 Explosives CAM VIII A ☐	TO-15 VOC CAM IX B ☐

Affirmative Responses to Questions A through F are required for "Presumptive Certainty" status		
A	Were all samples received in a condition consistent with those described on the Chain-of-Custody, properly preserved (including temperature) in the field or laboratory, and prepared/analyzed within method holding times?	☐ Yes ☐ No
B	Were the analytical method(s) and all associated QC requirements specified in the selected CAM protocol(s) followed?	☐ Yes ☐ No
C	Were all required corrective actions and analytical response actions specified in the selected CAM protocol(s) implemented for all identified performance standard non-conformances?	☐ Yes ☐ No
D	Does the laboratory report comply with all the reporting requirements specified in CAM VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data"?	☐ Yes ☐ No
E	VPH, EPH, APH, and TO-15 only a. VPH, EPH, and APH Methods only: Was each method conducted without significant modification(s)? (Refer to the individual method(s) for a list of significant modifications). b. APH and TO-15 Methods only: Was the complete analyte list reported for each method?	☐ Yes ☐ No ☐ Yes ☐ No
F	Were all applicable CAM protocol QC and performance standard non-conformances identified and evaluated in a laboratory narrative (including all "No" responses to Questions A through E)?	☐ Yes ☐ No
Responses to Questions G, H and I below are required for "Presumptive Certainty" status		
G	Were the reporting limits at or below all CAM reporting limits specified in the selected CAM protocol(s)?	☐ Yes ☐ No[1]
Data User Note: Data that achieve "Presumptive Certainty" status may not necessarily meet the data usability and representativeness requirements described in 310 CMR 40. 1056 (2)(k) and WSC-07-350.		
H	Were **all** QC performance standards specified in the CAM protocol(s) achieved?	☐ Yes ☐ No[1]
I	Were results reported for the complete analyte list specified in the selected CAM protocol(s)?	☐ Yes ☐ No[1]

[1] *All negative responses must be addressed in an attached laboratory narrative.*

I, the undersigned, attest under the pains and penalties of perjury that, based upon my personal inquiry of those responsible for obtaining the information, the material contained in this analytical report is, to the best of my knowledge and belief, is accurate and complete.

Signature:_____ **Position:**_____

Printed Name:_____ **Date:**_____

APPENDIX 4

1. Collecting and Preserving VPH Soil/Sediment Samples

2. Collecting and Preserving VPH Aqueous Samples

APPENDIX 4
Collecting and Preserving VPH Soil/Sediment Samples

OPTION 1: In-Field Methanol Preservation Technique

PERFORMANCE STANDARD: Obtain undisturbed soil/sediment sample and preserve with methanol at a ratio of 1 mL methanol per 1 gram soil/sediment.

Step 1: Choose appropriate sampling container:

60 mL wide mouth packer bottle; or
60 mL straight sided wide mouth bottle; or
60 mL VOC vial; or
40 mL VOC vial

All sampling containers should have an open-top screw cap with Teflon-coated silicone rubber septa or equivalent.

Step 2: (empty) Pre-label each container with a unique alpha/numerical designation. Obtain and record tare weight of each container to nearest 0.1 gram. *This information must be available to the laboratory performing the analyses.*

Step 3: Add 25 mL of purge-and-trap grade methanol to 60 mL containers, or add 15 mL of purge-and-trap grade methanol to 40 mL containers. *It is essential that the methanol be purge-and-trap grade or equivalent quality*. Immediately cap the container. Make a mark on the 60 mL containers approximately 15 mL above the level of methanol, or a mark on the 40 mL container approximately 10 mL above the level of methanol. The objective is to obtain 25 grams of soil/sediment in the 60 mL container, or 15 grams of soil/sediment in the 40 mL container, which is approximately 15 and 10 mL of soil/sediment volume, respectively, depending upon soil/sediment type and moisture content. Other masses of soil/sediment are permissible, as long as the ratio of [grams soil/sediment]/[mL methanol] is 1:1, ±25%. Store at 0-6ºC. *The use of a methanol trip blank prepared in this manner is recommended.*

Step 4: In the field, carefully add soil/sediment to the sample container, until the level of methanol in the vial reaches the designated volumetric mark. For wet soil/sediment, add slightly beyond the mark. IN NO CASE, HOWEVER, MAY THE LEVEL OF SOIL/SEDIMENT IN THE CONTAINER RISE ABOVE THE LEVEL OF METHANOL. The use of a 10-30 mL disposable syringe with the end cut off is recommended to obtain an undisturbed soil/sediment sample from freshly exposed soil/sediment samples. In such cases, obtain and extrude the soil/sediment into the sample container, avoiding splashing methanol out of the container.
Optional: Use a field electronic balance to ensure addition of desired mass of soil/sediment (25 grams to 60 mL containers, 15 grams to 40 mL containers).

Step 5: Use a clean brush or paper towel to remove soil/sediment particles from the threads of the sample container and screw cap. Tightly apply and secure screw cap. Gently swirl sample to break up soil/sediment aggregate, if necessary, until soil/sediment is covered with methanol. DO NOT SHAKE. Duplicate samples obtained in this manner are recommended. A split-sample must also be obtained for a determination of soil/sediment moisture content. This sample must NOT be preserved in methanol. HINT: fill this container 1/2 full, to allow screening of the sample headspace by the field investigator or the laboratory.

Step 6: Immediately place containers in cooler for storage in an upright position. Sample containers can be placed in separate zip-lock bags to protect containers in case of leakage during transport. Transport to analytical laboratory using appropriate chain-of-custody procedures and forms.

OPTION 2: Use of a Sealed-Tube Sampling/Storage Device

PERFORMANCE STANDARD: Obtain undisturbed soil sample and immediately seal in air-tight container, for shipment to laboratory and immersion in methanol within 48 hours.

Step 1: Obtain pre-cleaned and/or disposable samplers/containers that allow the collection and air-tight storage of at least 5-25 grams of soil.

Step 2: In the field, obtain an undisturbed sample from freshly exposed soil. Immediately seal container, and place in a cooler. Obtain a duplicate sample to enable the determination of soil moisture content (this does not need to be in a sealed sampler/container). Transport to analytical laboratory using appropriate chain-of-custody procedures and forms.

Step 3: Samples must be extruded and immersed in purge-and-trap (or equivalent) grade methanol at the laboratory within 48 hours of sampling, at a ratio of 1 mL methanol to 1 gram soil. In no case, however, shall the level of soil in the laboratory container exceed the level of methanol (i.e., the soil must be completely immersed in methanol).

NOTE: Documentation MUST be provided/available on the ability of the sampler/container to provide an air-tight seal in a manner that results in no statistically significant loss of volatile hydrocarbons for at least 48 hours.

SAFETY

Methanol is a toxic and flammable liquid, and must be handled with appropriate care. Use in a well-vented area, and avoid inhaling methanol vapors. The use of protective gloves is recommended when handling or transferring methanol. Vials of methanol should always be stored in a cooler with ice at all times, away from sources of ignition such as extreme heat or open flames.

APPENDIX 4
Collecting and Preserving VPH Aqueous Samples

MOST VPH/VOC AQUEOUS SAMPLES

All aqueous samples that will not be analyzed within 4 hours of collection must be preserved by pH adjustment, in order to minimize analyte losses due to biodegradation. For most samples, this can be accomplished by acidification of the sample to pH < 2, by adding 3-4 drops of 1:1 HCl to a 40 mL vial prior to collection. The sample should then be stored at 0-6ºC until it is analyzed. In lieu of acidification, samples may also be preserved with an appropriate base to pH > 11.0 (see below).

SAMPLES TO BE ANALYZED BY HEATED PURGE

ISSUE Traditionally, VPH and VOC aqueous samples have been preserved by addition of an acid (e.g., HCl) to lower the pH of the sample to less than 2.0. While this is still an acceptable approach for petroleum hydrocarbons and most VOCs, recent information and data have indicated that such a technique can lead to significant losses (up to 89%) of MTBE and other ethers (White, H., Lesnik, B., Wilson, J., *Analytical Methods for Fuel Oxygenates*, LUSTLINE Bulletin #42, New England Interstate Water Pollution Control Commission, 2002 (http://www.epa.gov/swerust1/mtbe/LL42Analytical.pdf). Specifically, the combination of a low pH and high temperature sample preparation technique (e.g., heated purge-and-trap) hydrolyze the ether bonds present in the sample, converting the ethers into alcohols (e.g., tert butyl alcohol).

PRESERVATION To prevent ether hydrolysis, samples should either (a) not be acidified or (b) not be heated. Because heating the sample may be necessary to achieve proper analyte purging/partitioning, an alternative to acidification is likely to be the most efficient means to prevent hydrolysis. Because ethers are not subject to base-catalyzed hydrolysis, raising the pH of the sample is an acceptable alternative to acidification. Studies by the USEPA have shown that preservation of aqueous samples to a pH greater than 11.0 using trisodium phosphate dodecahydrate will effectively prevent biological degradation of dissolved analytes, and will not result in deleterious effects on other dissolved oxygenates or on BTEX analytes.

PROTOCOL A recommended protocol to achieve a pH level > 11.0 is to add between 0.40 and 0.44 grams of trisodium phosphate dodecahydrate to a 40 mL vial prior to collection. For convenience, this can be done in the laboratory prior to sample collection in the field. Because it is more convenient to measure the required amount of trisodium phosphate dodecahydrate on a volume basis rather than by weight, the use of a pre-calibrated spoon is recommended. In the field, each vial is filled with the aqueous sample and sealed without headspace – as is traditionally done for acidified samples. The sample is then stored at 0-6ºC until it is analyzed.

NOTE If heated purge is used for the analysis of MTBE in aqueous samples, this is considered a significant modification as per Section 11.3.1 of the VPH methods. There would be no Presumptive Certainty for results obtained under this condition.

APPENDIX 5

SHIPPING METHANOL-PRESERVED SAMPLES

APPENDIX 5
Shipping Methanol Preserved Samples

Shipping of Hazardous Materials

Methanol is considered a hazardous material by the US Department of Transportation (DOT) and the International Air Transport Association (IATA). Shipments of methanol between the field and the laboratory must conform to the rules established in Title 49 of the Code of Federal Regulations (49 CFR parts 171 to 179), and the most current edition of the IATA Dangerous Goods Regulations. Consult these documents or your shipping company for complete details.

Small Quantity Exemption

The volumes of methanol recommended in the VPH methods fall under the small quantity exemption of 49 CFR section 173.4. To qualify for this exemption, all of the following must be met:

- ◊ the maximum volume of methanol in each sample container must not exceed 30 mL.
- ◊ the sample container must not be full of methanol.
- ◊ the sample container must be securely packed and cushioned in an upright position, and be surrounded by a sorbent material capable of absorbing spills from leaks or breakage of sample containers.
- ◊ the package weight must not exceed 64 pounds.
- ◊ the volume of methanol per shipping container must not exceed 500 mL.
- ◊ the packaging and shipping container must be strong enough to hold up to the intended use.
- ◊ the package must not be opened or altered while in transit.
- ◊ the shipper must mark the shipping container as follows:

"*This package conforms to 49 CFR 173.4"*

When shipping domestically by Federal Express via ground or air, the following rules apply:

- ◊ follow the inner packaging requirements of 49 CFR 173.4.
- ◊ no labels, placards, up arrows, or dangerous goods shipping papers are required.
- ◊ if the Federal Express airbill has a shippers declaration for hazardous goods on it, check the Yes box under *Shipper's Declaration not Required.*

When shipping internationally by Federal Express, the following rules apply*:*

- ◊ follow the inner packaging requirements of 49 CFR 173.4.
- ◊ use dangerous goods shipping papers.
- ◊ apply orientation arrows on opposite vertical sides on the exterior of the package.

Shipping Papers for International Shipments

International shipments must be accompanied by dangerous goods shipping papers that include the following:

Proper Shipping Name:	Methyl Alcohol
Hazardous Class:	Flammable Liquid
Identification Number:	UN1230
Total Quantity:	*(mL methanol/container x the number of containers)*
Emergency Response Info:	Methanol MSDS attached
Emergency Response Phone:	*provide appropriate number*
Shipping Exemption:	Dangerous Goods in Excepted Quantities

APPENDIX 6

VPH BY GC/PID/FID METHOD CALIBRATION AND ANALYSIS USING LINEAR REGRESSION

APPENDIX 6
VPH by GC/PID/FID Method Calibration and Analysis Using Linear Regression

Use of linear regression is permissible to calculate the slope and y-intercept that best describes the linear relationship between Target VPH Analytes or hydrocarbon range concentrations and instrument responses.

1. Prepare VPH Calibration Standards as described in Tables 2a and 2b at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 7.0. The VPH marker compounds for the C_5-C_8 aliphatic, C_9-C_{12} aliphatic and C_9-C_{10} aromatic ranges are presented in Table 5 of the method.

   Analyze each VPH Calibration Standard following the procedures outlined in Section 9.4. Tabulate area responses against the concentration purged. These data are used to calculate a calibration curve for each Target VPH Analyte (Equation 6-1). The correlation coefficient (r) of the resultant calibration curve must be ≥ 0.99.

Equation 6-1: Linear Regression: Target VPH Analytes

$$Area\ of\ peak = a \times concentration\ purged\ (\mu g/L) + b$$

where:

a =the calculated slope of the line
b = the calculated y intercept of the "best fit" line

A calibration curve may also be established for each aliphatic and aromatic hydrocarbon range of interest. Calculate the calibration curve for C_5-C_8 Aliphatic Hydrocarbons and C_9-C_{12} Aliphatic Hydrocarbons using the FID chromatogram. Calculate the calibration curve for the C_9-C_{10} Aromatic Hydrocarbons using the PID chromatogram. Tabulate the summation of the peak areas of all components in that hydrocarbon range (i.e., C_5-C_8 Aliphatic Hydrocarbons, 3 components) against the total concentration purged. These data are used to calculate a calibration curve for each VPH hydrocarbon range (Equation 6-2). The correlation coefficient (r) of the resultant calibration curve must ≥ 0.99.

Note: Do not include the area of any surrogates when determining the calibration curve for the hydrocarbon ranges. Do not include the area of naphthalene when determining the calibration curve for C_9 - C_{10} Aromatic Hydrocarbons.

Equation 6-2: Linear Regression: VPH Aliphatic and Aromatic Hydrocarbon Ranges

$$Area\ summation\ of\ range\ components = a \times total\ concentration\ purged\ (\mu g/L) + b$$

where:

a = the calculated slope of the line
b = the calculated y intercept of the "best fit" line

2. The concentration of a specific target analyte or hydrocarbon range may be calculated using linear regression analysis by applying Equation 6-3.

Equation 6-3: Determination of Target VPH Analytes and Hydrocarbon Range Concentrations using Linear Regression

$$Conc\ Analyte\ or\ HC\ Range\ (\mu g/L) = \left(\frac{A_x - b}{a} \right) \times D$$

where:

A_x = Response for the Target VPH Analyte or hydrocarbon range in the sample. Units are in area counts for Target VPH Analytes and the hydrocarbon ranges.
D = Dilution factor; if no dilution was made, D = 1, dimensionless.
a = Slope of the line for Target VPH Analyte or hydrocarbon range,
b = Intercept of the line for Target VPH Analyte or hydrocarbon range,

Note: Do not include the area of any surrogate standard in Ax when calculating a hydrocarbon range concentration.

3. **Conversion of µg/L to µg/kg**

To convert target analyte or hydrocarbon range results from µg/L into µg/kg, use Equations 7 and 9 in the VPH by GC/PID/FID method.

4. At a minimum, the working calibration curve must be verified on each working day, after every 20 samples, and at the end of the analytical sequence to verify instrument performance and linearity. The Percent Drift is determined using Equation 6-4. The Percent Drift for each Target VPH Analyte and surrogate must be ≤ 20. The Percent Drift for each hydrocarbon range must be ≤25. Greater Percent Drifts are permissible for n-nonane. If the Percent Drift for n-nonane is > 30, note the nonconformance in the case narrative. If more than one Target VPH Analyte or hydrocarbon range fails to meet the applicable criterion, the instrument must be recalibrated. Otherwise, sample analysis may proceed.

Equation 6-4: Percent Drift

$$\%Drift = \frac{Calculated\ concentration\ -Theoretical\ concentration}{Theoretical\ concentration}\ x\,100$$

APPENDIX 7

INITIAL DEMONSTRATION OF LABORATORY CAPABILITY FOR THE MassDEP VPH by GC/PID/FID METHOD

1.0 Overview of the Initial Demonstration of Laboratory Capability (IDLC) Approach

2.0 Demonstration of Acceptable System Background

3.0 Initial Demonstration of Accuracy (IDA)

4.0 Initial Demonstration of Precision (IDP)

5.0 Method Detection Limit (MDL)

For purposes of the IDLC accuracy and precision determinations (***and only this application***), the calibration mixture presented in Table 1 of the method is considered to be representative of Volatile Petroleum Hydrocarbon (VPH) Target VPH Analytes and hydrocarbon ranges (cumulative sum of the concentrations of the range calibration standards). Other reference materials or combinations of reference materials with an individual assay for individual Target VPH Analytes and the C_5 through C_8 aliphatic, C_9 through C_{12} aliphatic and C_9 through C_{10} aromatic ranges are also suitable for this determination.

1.0 Overview of the Initial Demonstration of Laboratory Capability (IDLC) Approach

An IDLC must be conducted to characterize instrument and laboratory performance prior to performing analyses using the VPH by GC/PID/FID Method. A laboratory may not report data to be used in support of MCP decisions unless the IDLC quality control requirements and performance standards described below and compiled in Table 7-2 of this Appendix are satisfied.

2.0 Demonstration of Acceptable System Background

Demonstration of acceptable system background is optional. To determine system background, a Laboratory Method Blank (LMB) is prepared and treated exactly as a typical field sample submitted for analysis, including exposure to all glassware, equipment, solvents and reagents. A LMB for aqueous sample analyses is prepared by adding a specified volume of surrogate spiking solution in purge-and-trap grade, or equivalent, methanol to organic-free water (ASTM Type I reagent grade). A LMB for soil/sediment sample analyses is prepared by adding a specified volume of "diluted" (to obtain the same on-column nominal concentration as above) surrogate spiking solution in purge-and-trap grade, or equivalent, methanol to organic-free water (ASTM Type I reagent grade). The volume of surrogate added should be the same as used for samples.

At least seven (7) replicate matrix-specific LMBs should be analyzed and the mean concentration of Target VPH Analytes and hydrocarbon ranges determined, as appropriate. Data produced (mean Target VPH Analyte and hydrocarbon range concentrations detected related to background noise) are used to assess instrument performance of a blank sample and evaluate potential contamination from the laboratory environment, in the absence of any other analytes or system contaminants. Calculate the measured concentration of C_{mean} of the replicate values as follows.

Equation 7-1: Calculation of C_{mean} LMB

$$C_{mean} = \frac{(C_1 + C_2 + C_3 + ...C_n)}{n}$$

where,

C_{mean} = Mean recovered concentration of the replicate LMB analysis.
C_1, C_2, ...C_n = Recovered concentrations of the replicate 1,2...n.
n = at least 7

Any concentration of C_{mean} that exceeds one half of the Reporting Limit (lowest Target VPH Analyte calibration or collective hydrocarbon range calibration standard) for either a Target VPH Analyte or hydrocarbon range is considered unacceptable, and indicates that laboratory and/or LMB contamination is present. The source of the non-conformance must be identified and corrected prior to conducting any sample analysis. For purposes of acceptable system background demonstration, concentrations are determined using Equations 6 and 8 in Section 9.6 of the VPH by GC/PID/FID Method for Target VPH Analytes and collective hydrocarbon ranges, respectively. Calculated concentrations below the lowest calibration standard, including zero (zero area), may be used in these calculations.

3.0 Initial Demonstration of Accuracy (IDA)

Prepare and analyze seven (7) replicate Laboratory Control Samples (LCSs) fortified at a concentration of 50% of the highest calibration curve standard (100 ug/L for aqueous samples and 5 mg/kg for soil/sediment samples). An LCS must be prepared and treated exactly as a typical field sample submitted for analysis, including exposure to all glassware, equipment, solvents and reagents. See Section 10.2.6 of the VPH by GC/PID/FID Method for how to prepare the LCS.

Calculate the mean measured concentration (C_{mean}) of the replicate LCSs for Target VPH Analytes and hydrocarbon ranges as follows.

Equation 7-2: Calculation of C_{mean}

$$C_{mean} = \frac{(C_1 + C_2 + C_3 + ...C_n)}{n}$$

where,

C_{mean} = Mean recovered concentration of the replicate analysis.
C_1, C_2, ...C_n = Recovered concentrations of the replicate 1,2...n.
n = 7

The value derived for C_{mean} must be within ± 30% of the true value or between 70 ug/L and 130 ug/L for aqueous samples and 3.5 mg/kg and 6.5 mg/kg for soil/sediment samples.

4.0 Initial Demonstration of Precision (IDP)

Using the results calculated from Section 3.0 above, calculate the percent relative standard deviation (%RSD) of the seven (7) replicate analysis, as indicated below. The %RSD must be $\leq$ 25 for both aqueous and soil/sediment samples.

Equation 7-3: Calculation of % RSD

$$\% \text{ RSD} = \frac{S_{n-1}}{C_{mean}} \text{ X } 100$$

where,

S_{n-1}= sample standard deviation (n-1) of the replicate analyses.
C_{mean} = mean recovered concentration of the replicate analysis.

5.0 Method Detection Limit (MDL)

The determination of the MDL for the MassDEP VPH by GC/PID/FID Method is optional. The reporting limit for the method is defined as the lowest calibration standard. Determination of the lowest detectable concentration of Target VPH Analytes and hydrocarbon ranges is verified on a continuing basis by analysis of the lowest concentration calibration standard and recovery of method surrogates. The recommended RL concentrations for the VPH by GC/PID/FID Method do not approach (are considerably higher than) the sensitivity limits of the VPH by GC/PID/FID Method for either Target VPH Analytes or hydrocarbon ranges and are more than adequate to meet the most stringent regulatory requirements of the MCP.

An MDL may be established for Target VPH Analytes and hydrocarbon ranges either analytically using the 40 CFR 136 approach or by the statistical evaluation of analytical system noise as a good laboratory practice component of an overall quality control program for the VPH by GC/PID/FID Method.

5.1 Determination of MDL, 40 CFR 136, Appendix B Approach

To determine MDL values, take seven replicate aliquots of reagent water fortified at the estimated or "calculated" MDL concentration determined in Equation 7-6 below or the concentration of the lowest calibration standard, and process through the entire analytical method over a three day period. These seven MDL replicate analyses may be performed gradually over a three day period or may represent data that have been collected, at a consistent MDL "calculated" concentration, over a series of more than three days. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

Equation 7-4: Calculation of MDL based on Laboratory Analysis

$$MDL = (t_{n-1}) \times (S_{n-1})$$

where,

t_{n-1} = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t_{n-1} = 3.14 for seven replicates]
S_{n-1} = Sample standard deviation (n-1) of 7 replicate MDL analyses (equivalent to a "low-level" LCS)

5.2 Determination of MDL and Limit of Quantitation (LOQ) by Statistical Evaluation of System Noise

Seven (7) replicate aliquots of a System Solvent Blank (SSB) must be prepared and analyzed exactly as a typical field sample submitted for analysis, including exposure to all glassware, equipment, solvents and reagents. A SSB for water analyses is prepared by adding 5 uL of purge-and-trap grade, or equivalent, methanol to 5 mL of organic-free water (ASTM Type I reagent grade). A SSB for soil/sediment analyses is prepared by adding 100 uL purge-and-trap grade, or equivalent, methanol to 4.9 mL of organic-free water (ASTM Type I reagent grade).

Data produced are used to assess the level of noise and the baseline rise attributable solely to the GC/PID/FID system, in the absence of any other analytes or system contaminants. These data are used to calculate the LOQ and MDL using the Keith statistical approach. ***For these analyses, the data system's threshold for peak area integration must be adjusted to ensure that a positive value is recorded for the Target VPH Analytes and hydrocarbon ranges of interest, as practical.*** Tabulate the area responses for each Target VPH Analyte and hydrocarbon range. Calculate the LOQ and MDL using Equations 7-5 and 7-6, respectively. An example LOQ and MDL calculation for the VPH aliphatic and aromatic hydrocarbon ranges for an aqueous sample is presented below in Table 7-1.

Equation 7-5: Calculation of Limit of Quantitation (LOQ)

$$LOQ_x = 10 * S_{x,n-1} CF_x$$

$S_{x,n-1}$ = Sample standard deviations for peak areas of Target VPH Analytes and hydrocarbon ranges of interest for the seven (7) replicate SSBs reported in appropriate units.

CF_x = Representative CF for appropriate Target VPH Analytes or hydrocarbon range

Equation 7-6: Calculation of MDL

$$MDL = LOQ/3$$

Table 7-1 LOQ Sample Calculation for Seven (7) System Solvent Blanks (SSBs) – VPH Hydrocarbon Ranges Only

Replicate Number	VPH Hydrocarbon Range (Area Units)		
	C_5 - C_8 aliphatic	**C_9 - C_{12} aliphatic**	**C_9 - C_{10} aromatic**
1	32887	41407	18427
2	54035	26628	18294
3	10991	38536	17885
4	19382	12497	20846
5	9730	32572	14570
6	37624	11564	18709
7	87050	15501	16545
Range Average	24765	25529	17892
Calculations:			
Range $S_{x, n-1}$	15994	11573	1801
Range CF (ug/L * AU^{-1})	0.00010	0.00007	0.00003
LOQ (ug/L)	16	8.1	0.5
MDL (ug/L)	5.3	2.7	0.17

Table 7-2 Initial Demonstration Of Laboratory Capability QC Requirements

Reference Section	Requirement	Specification & Frequency	Acceptance Criteria
2.0	Initial Demonstration of Acceptable System Background (Optional)	Analyze at least 7 replicate Laboratory Method Blanks (LMB) fortified with surrogate spiking solution. Calculate the mean recovered concentration for each Target VPH Analyte and hydrocarbon range. See Equation 7-1 in Section 2.0.	The mean LMB concentrations must be < ½ of the RL (lowest point on calibration curve or lowest cumulative range calibration standard).
3.0	Initial Demonstration of Accuracy (IDA)	Analyze 7 replicate LCSs fortified with VPH calibration standards at a nominal concentration of 100 ug/L or 5 mg/kg for each standard analyte. Calculate the mean recovered concentration (C_{mean}) for each Target VPH Analyte and hydrocarbon range. See Equation 7-2 in Section 3.0.	The C_{mean} must be ± 30% of the true value of the aliphatic and aromatic hydrocarbon ranges and Target VPH Analytes for both aqueous and soil/sediment samples.
4.0	Initial Demonstration of Precision (IDP)	Calculate the percent relative standard deviation (%RSD) of LCS replicates in Section 3.0 for each Target VPH Analyte and hydrocarbon range. See Equation 7-3 in Section 4.0.	The %RSD must be ≤ 25% for both aqueous and soil/sediment samples.
5.0	Method Detection Limit (MDL) Determination (Optional)	Select a fortifying level at the estimated or "calculated" MDL or RL for the LCS. See Equation 7-6 in Section 5.2. Analyze these 7 replicate "low-level" LCSs over multiple days and calculate the MDL using Equation 7-4 in Section 5.1. Do not subtract any blank contribution to this value. MDLs may also be determined by a statistical evaluation of system noise based on the analysis of seven (7) system solvent blanks (SSB). See Section 5.2.	See 40 CFR 136, Appendix B. The MDL must be < ½ of the RL for individual Target VPH Analytes and < ½ of the RL for collective VPH hydrocarbon ranges (See Section 12.0 of the method).