METHOD FOR THE DETERMINATION OF

VOLATILE PETROLEUM HYDROCARBONS (VPH) BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Massachusetts Department of Environmental Protection

Bureau of Waste Site Cleanup

Commonwealth of Massachusetts

Executive Office of Energy and Environmental Affairs
Matthew A. Beaton
Secretary

Department of Environmental Protection
Martin Suuberg
Commissioner

January 2017
Revision 0

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:

Quantitation vs. Extracted vs. Total Ions:

- Quantitation Ions are used to quantify the concentrations of specific individual Target VPH Analytes (e.g., benzene, toluene, etc.) in the same manner as conventional EPA GC/MS methods (e.g., EPA Method 8260).
- Extracted Ions (m/z 120 and 134) are used to identify and quantify collective area counts for C_9-C_{10} Aromatic Hydrocarbons; a collective range concentration (µg/L) is then calculated using a Relative Response Factor (RRF) derived from the analysis of a calibration standard containing a mixture of specified C_9-C_{10} aromatic hydrocarbon compounds.
- The Total Ion Chromatogram is used to determine collective ranges of aliphatic hydrocarbons, initially by quantifying the collective area counts of all hydrocarbons within specified ranges (i.e., C_5-C_8 and C_9-C_{12}), calculating range concentration values (µg/L) using RRFs, and then subtracting the concentrations of Target VPH Analytes and C_9-C_{10} Aromatic Hydrocarbons that elute within the range of interest.

Peak Integration Techniques:

- For individual Target VPH Analytes, the quantitation ion peak is integrated in the same manner as conventional EPA GC/MS methods (e.g., EPA Method 8260). 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 total ion chromatogram 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, extracted ions m/z 120 and 134 are 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 internal and surrogate standards, the total ion peaks are individually integrated (valley to valley), so that their areas can be subtracted from the collective areas of the hydrocarbon ranges discussed above.

Calibration Approach:

- The RRFs for the aliphatic hydrocarbon ranges are based on the correlation of collective total ion area counts to the collective concentration values of a specified mixture of aliphatic hydrocarbon standards, in which the collective total ion area count is determined via the summation of individual valley-to-valley total ion peaks for the individual standards.
- For the aromatic range (i.e., C_9-C_{10} Aromatic Hydrocarbons), the RRF is based on the correlation of collective extracted ion area counts to the collective concentration values of a specified mixture of aromatic hydrocarbon standards, in which the collective extracted ion area count is determined via the summation of individual valley-to-valley extracted ion peaks for the individual standards.

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 total or extracted ion 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 RRF 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 internal and 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 total ion area count for a specified aliphatic range (i.e., C_5-C_8 or C_9-C_{12}), it is necessary to subtract the individual (valley-to-valley) total ion peak areas of internal and surrogate standards that elute within that range. This is not an issue for the C_9-C_{10} Aromatics, as the range area count is based upon extracted ions, which will not be present in the internal or surrogate standards.

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

For additional information and insights on the origin and implications of the various requirements and biases within this method, and to see how it compares to the MassDEP VPH by GC/PID/FID method, 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

METHOD FOR THE DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (VPH) BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

TABLE OF CONTENTS

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement by the Massachusetts Department of Environmental Protection (MassDEP). Trade names and commercial products specified within this method are based upon their use in validation studies conducted by MassDEP. Equipment and materials cited in this method may be replaced by similar products, as long as adequate data exist or have been produced documenting equivalent or superior performance.

LIST OF ACRONYMS

amu	Atomic Mass Unit
APH	Air-Phase Petroleum Hydrocarbons
ASTM	American Society for Testing and Materials
BFB	4-Bromofluorobenzene
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CAM	Compendium of Analytical Methods
%D	Percent Difference
DF	Dilution Factor
eV	Electron Volts
FID	Flame Ionization Detector
GC/MS	Gas Chromatography / Mass Spectrometry
HCl	Hydrochloric Acid
ICV	Initial Calibration Verification
I.D.	Internal Diameter
IDLC	Initial Demonstration of Laboratory Capability
IS	Internal Standard
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
LMB	Laboratory Method Blank
MassDEP	Massachusetts Department of Environmental Protection
m/z	Mass-to-charge ratio
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
RRF	Relative Response Factor
RRT	Relative Retention Time
%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.

METHOD FOR THE DETERMINATION OF
VOLATILE PETROLEUM HYDROCARBONS (VPH)
BY GAS CHROMATOGAPHY/MASS SPECTROMETRY (GC/MS)

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 aqueous 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 mass spectrometer (MS) detector. It should be used by, or under the direct supervision of, analysts experienced in the use of purge-and-trap systems and GC/MS instrumentation for the identification and quantification of contaminant concentrations in aqueous and soil/sediment matrices.

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 previously issued by the agency in January 1998, and updated (Revision 1.1) in May 2004, and involves the use of flame ionization and photoionization detectors (FIDs and PIDs). The method detailed in this document is identified as "MassDEP VPH by GC/MS." The other option is identified as "MassDEP VPH by GC/PID/FID." 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 GC/MS.

1.5 In addition to the quantification of aliphatic and aromatic hydrocarbon ranges, the MassDEP VPH by GC/MS method is also designed to directly 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.

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 > 220ºC.

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 2. The format of these reports is left to the discretion of 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).

1.10 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 by GC/MS Method 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).

1.11 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 on the MassDEP Analytical Protocol Certification Form (See Appendix 2, 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 3.5 through 3.7 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 method and procedural modifications are fully documented in a detailed standard operating procedure (SOP).

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

1.13 This method should be used in conjunction with the current version of WSC-CAM-IV C, "Quality Control Requirements and Performance Standards for the Analysis of Volatile Petroleum Hydrocarbons (VPH) by Gas Chromatography/Mass Spectrometry (GC/MS) in Support of Response Actions Under the Massachusetts

Contingency Plan (MCP)". WSC-CAM-IV C was developed by MassDEP to complement this MassDEP VPH by GC/MS Method and to provide more detailed guidance regarding compliance with the QC requirements and performance standards of the MassDEP VPH by GC/MS Method.

2.0 SUMMARY OF METHOD AND DATA QUALITY OBJECTIVES

2.1 Samples are analyzed using purge-and-trap sample concentration. The gas chromatograph 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 mass spectrometer. Target VPH Analytes are identified and quantified using characteristic ions. Collective concentrations of C_9-C_{10} aromatic hydrocarbons are quantified using extracted ions. Collective concentrations of aliphatic hydrocarbon ranges are quantified using the total ion chromatogram.

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/MS. 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/MS.

2.3 This method is based on (1) USEPA Methods 5030B, 5035A, 8000D, and 8260B, SW-846, "Test Methods for Evaluating Solid Waste," (2) MassDEP Method for the Determination of Volatile Petroleum Hydrocarbons (VPH), Revision 1, May 2004 and (3) MassDEP Method for the Determination of Air-Phase Petroleum Hydrocarbons (APH), Revision 1, December 2009.

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 and non-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 **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.

3.4 **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.

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

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

3.7 **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. 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 extracted ions 120 and 134.

3.8 **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.

3.9 **Initial Calibration Verification (ICV) Standard** is defined as a mid-range standard prepared from a separate source than used for the initial and continuing calibration standards. This analysis must be performed every time an initial calibration is performed.

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 and internal standards 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 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 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 25 component mixture of the aliphatic and aromatic compounds listed in Table 1. The compounds comprising the VPH Component Standard are used to (a) define the individual retention times and response 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 response 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 Methods for Evaluating Solid Waste: Physical/Chemical Methods," 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 laboratory method blank 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 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. When requested by the data user, the identification of such non-VPH compounds must be disclosed on the laboratory report form or laboratory narrative. See Table 9 for a list of potential non-petroleum compounds which may contribute to hydrocarbon range concentrations.

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 Except as specified below, one of the following traps is required:

- VOCARB 3000 (Carbopack B/Carboxen-1000/Carboxen-1001); or
- Tekmar #9 Trap (proprietary sorbent).

Whichever trap is employed, it must demonstrate sufficient sorption and desorption characteristics to meet the RLs of all Target VPH Analytes and the QC requirements in this method. The trap must also be capable of desorbing the late-eluting target analytes.

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. Substitution of one of the required traps is not allowed, unless it can 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 2).

To demonstrate equivalency of trap desorption efficiency, a neat gasoline standard must be analyzed using one of the required traps 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 $\leq$ 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 gas chromatograph for use with a capillary column is required.

6.2.2 Chromatographic Column: Except as specified below, one of the following columns is required:

- 30 m x 0.25 mm internal diameter (I.D.) VOCOL™ with 1.5 micron film thickness; or
- 30 m x 0.25 mm I.D. RTX-502.2™ with 1.4 micron film thickness.

It should be noted that both columns listed above exhibit the following co-elution:

- m-Xylene and p-Xylene

This co-elution does not interfere with the ability of the method to quantify and identify hydrocarbon ranges or Target VPH Analytes.

NOTE: Based upon data obtained from the original 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 quantification of aliphatic and aromatic compounds within the collective hydrocarbon ranges specified in the method. Substitution of one of the required columns 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 2).

To demonstrate equivalency of column chromatography, a neat gasoline standard must be analyzed on one of the required columns 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 hydrocarbon ranges and Target VPH Analytes must be determined for each column. 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 Mass Spectrometer System

6.3.1 The mass spectrometer must be set to scan from 35 to 250 atomic mass units (amu), at a minimum, every three seconds or less, utilizing 70 electron volts (eV) in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when at least 50 ng of 4-bromofluorobenzene (BFB) is injected.

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. 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°C, 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 3a and 3b provide recommended concentrations for each calibration standard for a 5-point initial calibration of hydrocarbon ranges and Target VPH Analytes.

Aqueous standards are not stable and should be discarded after one hour.

7.5 Surrogate Standards

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 surrogate standards. The surrogate standards are included in the VPH calibration standards. The recommended surrogate standard is toluene-d8, which does not coelute with the 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 Internal Standards

The use of three internal standards (IS) is required. The recommended internal standards are Fluorobenzene (or 1,4-Difluorobenzene), Chlorobenzene-d5 and 1,4-Dichlorobenzene-d4. Stock standards of these compounds should be prepared or purchased at a concentration of 50 µg/mL. The volume of internal standard mixture added for each analysis must be the same from run to run. The concentration of internal standard in all samples, standards, and QC samples should be 50 µg/L (2.5 mg/kg).

7.7 GC/MS Tuning Standard

The required MS tuning standard is BFB. Stock standards of BFB should be prepared or purchased at a concentration of 25 ug/mL.

7.8 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.

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 0-6ºC 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 0-6ºC 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 3.

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 0-6ºC 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 0-6ºC 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 3.

8.2.3 The desired ratio of methanol-to-soil/sediment is 1 mL methanol/1 gram soil/sediment, $\pm$ 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 4 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 0-6ºC 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 4.

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

- 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 valves.

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

If the purge-and trap autosampler is utilized:

- The addition of internal standards and 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 6. 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/MS 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 minutes, 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 grams 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, add a specified volume (recommended 5-10 µL) of the internal standard spiking solution through the valve bore of the syringe to yield a final concentration of 2.5 mg/kg. If an autosampler is used, the addition of internal standard may be performed automatically by the autosampler.

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

9.1.3.10 Complete operations as specified in Paragraphs 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 grams 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 14). 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/MS Conditions: Refer to Section 10.2.1 for peak resolution requirements.

1. Recommended GC oven program: 30 m x 0.25 mm I.D. VOCOL™ with 1.5 µm film thickness: initial temperature 40°C, hold for 2.0 minutes. Increase temperature to 125°C at 7.0°C/min, and then increase temperature to 230°C at 12°C/min. Hold for 3.0 minutes. (NOTE: Conditions described are for an Agilent 6890/5973 GC/MS system).

2. Recommended GC oven program: 30 m x 0.25 mm I.D. RTX-502.2™ with 1.4 µm film thickness: initial temperature 50°C, hold for 5.0 minutes. Increase temperature to 130°C at 11°C/min, and then increase temperature to 250°C at 20°C/min. Hold for 1.0 minute. (NOTE: Conditions described are for an Agilent 7890/5975 GC/MS system).

	(1)VOCOL™	**(2)RTX-502.2™**
Gas Flows: Helium carrier gas	1.5 mL/min	1.0 mL/min
Recommended Sample Injection		
Injection mode	Split 30:1	Split (may vary)
Injection port temperature	150°C	240°C
Inlet pressure	11.85 psi	7.9 psi
Purge flow	40 mL/min	20 mL/min
Gas saver flow	20 mL/min (on at 7 min)	10 mL/min
Recommended MS Conditions		
Temperature of MS transfer line	230°C	250°C
Temperature of MS Quad	150°C	150°C
Temperature of MS Source	230°C	200°C
Solvent Delay	1 minute	3 minutes

9.3 Retention Time Windows

The retention time (Rt) window for 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 minutes before the elution of naphthalene.

VPH marker compounds and windows are summarized in Table 5.

9.4 Calibration

9.4.1 Daily GC/MS Performance Check

A check of the GC/MS tuning must be performed daily every 12 hours prior to sample analyses. The GC/MS system is checked to confirm that acceptable performance criteria for mass spectral ion abundance ratios are met for BFB. These criteria must be met prior to analyzing any additional standards, blanks and samples.

Performance criteria for the required tuning standard, BFB, are provided in Table 2. If the tuning criteria are not met, the GC/MS must be retuned and the analysis repeated.

9.4.2 The VPH calibration standards are used to calibrate the GC/MS system. Two distinct calibration operations are necessary.

9.4.2.1 Target VPH Analytes and Surrogate: Relative Response Factors (RRFs) are calculated for the Target VPH Analytes and surrogate standard, based upon a correlation between the concentration of analyte/surrogate and area counts for the relevant quantitation ions. This allows for the individual identification and quantitation of these specific compounds. It is not necessary to develop response factors for any other individual VPH Components.

9.4.2.2 Collective Aliphatic/Aromatic Hydrocarbon Ranges: RRFs 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 ion area count. An RRF is calculated for C_9-C_{10} aromatic hydrocarbons based upon a correlation between the TOTAL concentration of aromatic VPH Components eluting within this range and the total area count of extracted ions 120 and 134. Specified VPH Components are designated marker compounds to define the beginning and end of the hydrocarbon ranges (see Table 5).

9.4.2.3 Primary (quantitation) and secondary extracted ions for all VPH Components and the recommended surrogate and internal standards are provided in Table 7. The recommended internal standards used for quantitation of each Target VPH Analyte, surrogate and hydrocarbon range are provided in Table 8. A listing of the hydrocarbon range compounds used to establish response factors for each hydrocarbon range of interest and their individual component concentration (µg/L) is provided in Table 3b.

9.4.3 Initial Calibration

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

9.4.3.2 The use of RRFs 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 9.4.3.12 and 9.4.3.13). 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.

NOTE: A sample calculation demonstrating the proper application of the equations shown in the following sections is presented in Appendix 5, VPH by GC/MS Method Calculations.

9.4.3.3 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 3a and 3b, 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 an RRF for the surrogate.

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

9.4.3.5 Target VPH Analytes and Surrogate - Tabulate the area response of the primary (or quantitation) ions against the concentration for each Target VPH Analyte and internal standard, and calculate an RRF for each compound using Equation 1. Perform this calculation for each Target VPH Analyte and the surrogate.

Equation 1: Relative Response Factor for Target VPH Analytes and Surrogate

$$RRF = [(A_{EC}) * (C_I)] / [(A_{EI}) * (C_C)]$$

where:

RRF = relative response factor
A_{EC} = area count of the primary (quantitation) ion for the analyte of interest
C_I = concentration of the associated internal standard (µg/L): See Section 7.6
A_{EI} = area count of the primary (quantitation) ion for the associated internal standard
C_C = concentration of analyte of interest (µg/L)

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

9.4.3.7 Calculate an RRF for the C_5-C_8 aliphatic hydrocarbon range using the following steps.

Using total ion integration, sum the **individual peak areas** of the six VPH Components that are used to establish an average range RRF for C_5-C_8 aliphatic hydrocarbons, as designated in Table 3b. Do not include the peak areas of internal standards or surrogates which elute within this range. 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.

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

Equation 2: Relative Response Factor for C_5-C_8 Aliphatic Hydrocarbons

$$\text{Range } RRF = [(A_T) * (C_I)] / [(A_{EI}) * (C_T)]$$

where:

A_T = total ion area count of the six aliphatic VPH Components which elute within this range (see Table 3b)
C_T = summation of the concentrations of the six aliphatic VPH Components (µg/L) which elute within this range: refer to the last column of Table 3b

9.4.3.8 Calculate an RRF for the C_9-C_{12} aliphatic hydrocarbon range using the following steps.

Using total ion integration, sum the **individual peak areas** of the six VPH Components that are used to establish an average range RRF for C_9-C_{12} aliphatic hydrocarbons, as designated in Table 3b. Do not include the peak areas of internal standards or surrogates which elute within this range. 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.

Using this total area, calculate the C_9-C_{12} hydrocarbon range RRF using Equation 3.

Equation 3: Relative Response Factor for C_9-C_{12} Aliphatic Hydrocarbons

$$\text{Range } RRF = [(A_T) * (C_I)] / [(A_{EI}) * (C_T)]$$

9.4.3.9 Calculate an RRF for the C_9-C_{10} aromatic hydrocarbon range using the following steps.

(1) Using extracted ion mass-to charge ratio (m/z) 120, sum the **individual peak areas** of the five VPH Components that are used to establish an average range RRF for C_9-C_{10} aromatic hydrocarbons, as designated in Table 3b. 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.

(2) Using extracted ion m/z 134, sum the **individual peak areas** of the five VPH Components that are used to establish an average range RRF for C_9-C_{10} aromatic hydrocarbons, as designated in Table 3b. 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.

Sum the area counts from (1) and (2) above.

Using this total area, calculate the C_9-C_{10} aromatic range RRF using Equation 4.

Equation 4: Relative Response Factor for C_9-C_{10} Aromatic Hydrocarbons

$$\text{Range } RRF = [(A_T) * (C_I)] / [(A_{EI}) * (C_T)]$$

where:

A_T = summation of area counts for extracted ions 120 and 134 for the five aromatic VPH Components which elute within this range (see Table 3b)

C_T = summation of the concentrations of the five aromatic VPH Components (µg/L) which elute within this range: refer to the last column of Table 3b

9.4.3.10 Calculate the average RRF for each of the Target VPH Analytes, the surrogate, and each hydrocarbon range.

9.4.3.11 Calculate the percent relative standard deviation (%RSD) of the RRFs over the working range of the curve for each of the Target VPH Analytes, the surrogate, and each hydrocarbon range using Equation 5.

Equation 5: Percent Relative Standard Deviation

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

where:

%RSD = percent relative standard deviation

SD_{n-1} = standard deviation (n-1 degrees of freedom)

AVG_x = average RRF from the initial calibration curve

9.4.3.12 If the %RSD is ≤20 for Target VPH Analytes and the surrogate and ≤25 for hydrocarbon ranges, linearity can be assumed for the associated Target VPH Analyte, the surrogate, and hydrocarbon range, respectively.

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.

9.4.3.13 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.

9.4.3.14 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.

9.4.3.15 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 of each Target VPH Analyte and hydrocarbon range using Equation 6. Percent recoveries must be between 70-130%. Recalibrate if >10% of all analytes are outside of criteria.

Equation 6: 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)

9.4.4 Continuing Calibration

9.4.4.1 A Continuing Calibration Standard must be analyzed daily every 12 hours prior to sample analysis. It should be noted that the Percent Differences (%Ds) are calculated (Equation 7) when RRFs 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.

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

9.4.4.3 Calculate the RRF for each Target VPH Analyte, surrogate, and hydrocarbon range from the Continuing Calibration Standard using Equations 1 through 4.

9.4.4.4 Calculate the %D of the Continuing Calibration Standard RRF from the initial calibration average RRF using Equation 7.

Equation 7: Percent Difference

$$\%D = [(RRF_C) - (RRF_I)]/[(RRF_I)]*100$$

where:

%D = Percent Difference
RRF_C = RRF from the VPH Continuing Calibration Standard
RRF_I = average RRF from the initial calibration curve

9.4.4.5 The %D or Percent Drift for each Target VPH Analyte, surrogate, and hydrocarbon range must be $\leq$ 20. 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.

9.4.5 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. The marker compounds used for each range are defined in Table 5.

9.5 GC/MS Analysis of Samples

9.5.1 Samples are analyzed in a group referred to as an analytical batch. The analytical sequence begins with instrument tune and calibration (initial or continuing) followed by analysis of samples interspersed with blanks and QC samples (for a maximum of 12 hours). The analytical sequence ends when any required qualitative and/or quantitative QC criteria are exceeded or when 12 hours have passed, whichever comes first.

9.5.2 Identification of Target VPH Analytes

The Target VPH Analytes in field samples must be identified by a qualified mass spectrometrist competent in the interpretation of chromatograms and mass spectra.

If the Target VPH Analyte concentration is above the RL, the laboratory **must** report it if the following criteria are met:

(1) The relative retention time (RRT) of the target analyte in the sample agrees with the RRT of the target analyte in the associated Continuing Calibration Standard within $\pm$ 0.33 minutes; and

(2) The relative intensities of the primary (quantitation) and secondary ions (Table 7) for the target analyte in the sample agree within ±20% of the relative intensities of the same ions in the Continuing Calibration Standard.

If co-elution of interfering components prohibits accurate identification of the sample component RRT from the total ion chromatogram, the RRT should be assigned using extracted ion current profiles for the ion unique to the component of interest.

If the above-referenced criteria are met but in the analyst's opinion a false positive result is suspected, this must be reported and explained in the laboratory narrative.

For comparison of the target analyte's mass spectra between samples and standards, mass spectra of standards obtained on the GC/MS under the same instrument conditions are required (e.g., from the calibrations). Once obtained, these standard spectra must be used for identification and reference purposes.

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, surrogate compounds, and internal standards, 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, surrogate compounds, and internal standards.

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 responses 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 hydrocarbon 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 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.

<u>Analytical Note</u>: 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 RRFs 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 RRF from the initial calibration is used to calculate the concentration of an analyte or surrogate detected in the sample. Equation 8 is used to calculate the concentration of Target VPH Analytes and the surrogate in µg/L.

Equation 8: Aqueous Samples: Calculation of Sample Concentration (µg/L)

$$Cx = \{ [(A_x) * (C_{IS})]/[(A_{IS}) * (RRF_{avg})] \} * DF$$

where:

Cx= concentration of target analyte, µg/L
Ax = area of primary (quantitation) ion for the Target VPH Analyte (see Table 7)
C_{IS} = concentration of the associated internal standard, µg/L: See Section 7.6
A_{IS} = area of primary (quantitation) ion for the associated internal standard (see Table 7)
RRF_{avg} = average RRF for the Target VPH analyte to be measured
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 14 through 16)

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

9.6.2 Hydrocarbon Ranges

When calculating the VPH by GC/MS 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 internal standards, surrogates and Target VPH Analytes, as described below in Sections 9.6.2.1, 9.6.2.2, and 9.6.2.3.

The average hydrocarbon range RRF 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).**

At the discretion of the data user, the contribution of non-VPH compounds (compounds not meeting the definitions in Sections 3.5, 3.6 and 3.7) that elute within the method-defined retention time windows for the aliphatic and aromatic hydrocarbon ranges may be excluded from collective hydrocarbon range concentration calculations. Specifically, the total ion area counts (aliphatic ranges) and the 120/134 m/z area counts (aromatic range) for these non-VPH compounds may be excluded provided the compound is **positively identified** by GC/MS. However, if the non-VPH compound co-elutes with an aliphatic petroleum hydrocarbon, the total ion area count cannot be subtracted from the range. In addition, in complex sample matrices (i.e., many co-eluting peaks, complex petroleum patterns), this type of data adjustment may not be possible. All data adjustments and the presence of these non-VPH compounds must be disclosed on the laboratory report form and laboratory narrative. A list of common non-VPH compounds that elute within the aliphatic and aromatic ranges is presented in Table 9.

Detailed guidance regarding the identification criteria for these non-VPH compounds is presented in Section 11.4.

9.6.2.1 C_5-C_8 Aliphatic Hydrocarbons

- Using total ion integration, sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 5.
- From this sum, subtract the total ion area counts of all internal standards and surrogates which elute in this range.
- Calculate a preliminary concentration (Unadjusted C_5-C_8 aliphatic hydrocarbons) in µg/L using Equation 10.

Equation 10: Aqueous Samples: Calculation of Preliminary (Unadjusted) Sample Concentration of C_5-C_8 Aliphatic Hydrocarbons (µg/L)

$$Cx = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})] * DF$$

where:

Cx=	concentration of hydrocarbon range, µg/L
A_x =	total ion area count of all peaks eluting within aliphatic hydrocarbon range window (excluding the surrogates and internal standards)
C_{IS} =	concentration of the associated internal standard (µg/L): See Section 7.6
A_{IS} =	area count of the primary (quantitation) ion for the associated internal standard
RRF_{avg} =	average RRF for C_5-C_8 aliphatic hydrocarbons
DF =	dilution factor (see Section 9.5.7)

For soil/sediment samples, convert the µg/L value to µg/kg using Equation 11.

Equation 11: 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 10 (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 14 through 16)

NOTE: These values are reported as the "Unadjusted C_5-C_8 aliphatics" as shown in Appendix 2, 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 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 2, Exhibit 1.

9.6.2.2 C_9-C_{10} Aromatic Hydrocarbons

- Using extracted ion m/z 120, sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 5.
- Using extracted ion m/z 134, sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 5.
- Sum the area counts of extracted ions m/z 120 and 134 from the above two steps.
- Calculate the concentration in µg/L using Equation 12.

Equation 12: Aqueous Samples: Calculation of Sample Concentration of C_9-C_{10} Aromatic Hydrocarbons (µg/L)

$$Cx = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})] * DF$$

where:

Cx= concentration of hydrocarbon range, µg/L
A_x = sum of area counts of extracted ions m/z 120 and 134
C_{IS} = concentration of the associated internal standard (µg/L): See Section 7.6
A_{IS} = area count of the primary (quantitation) ion for the associated internal standard
RRF_{avg} = average RRF for C_9-C_{10} aromatic hydrocarbons
DF = dilution factor (see Section 9.5.7)

For soil/sediment samples, convert the µg/L value to µg/kg using Equation 11.

9.6.2.3 C_9-C_{12} Aliphatic Hydrocarbons

- Using total ion integration, sum all peaks in the appropriate retention time window, as specified in Section 9.3 and Table 5.
- From this sum, subtract the total ion area counts of all internal standards and surrogates which elute in this range.
- Calculate a preliminary concentration (Unadjusted C_9-C_{12} aliphatic hydrocarbons) in µg/L using Equation 13.

Equation 13: Aqueous Samples: Calculation of Preliminary (Unadjusted) Sample Concentration of C_9-C_{12} Aliphatic Hydrocarbons (µg/L)

$$Cx = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})] * DF$$

where:

Cx=	concentration of hydrocarbon range, µg/L
A_x =	total ion area count of all peaks eluting within aliphatic hydrocarbon range window (excluding the surrogates and internal standards)
C_{IS} =	concentration of the associated internal standard (µg/L): See Section 7.6
A_{IS} =	area count of the primary (quantitation) ion for the associated internal standard
RRF_{avg} =	average RRF for C_9-C_{12} aliphatic hydrocarbons
DF =	dilution factor (see Section 9.5.7)

For soil/sediment samples, convert the µg/L value to µg/kg using Equation 11.

NOTE: These values are reported as the "Unadjusted C_9-C_{12} aliphatics" as shown in Appendix 2, 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 and the Target VPH Analytes 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 2, 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 9.1.6. Using the data obtained from Section 9.1.6, W_d is calculated using Equations 14 through 16.

Equation 14: Percent Moisture

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

Equation 15: Percent Solids

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

Equation 16: Dry Weight of Sample

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

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 17: Calculation of Solvent/Water Volume

mL solvent/water (Vt) = mL of methanol + ((% moisture/100) × g of sample)

This "corrected" Vt value should be substituted directly for the Vt value shown in Sections 9.6.1 and 9.6.2, Equations 9 and 11. It should be noted that whether corrected or uncorrected, the Vt value used in Equations 9 or 11 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 (every 12 hours), a tune, an Initial Calibration or Continuing Calibration Standard, LMB, LCS, and LCS Duplicate must be analyzed. The tune, 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.

10.1.3 The recommended sequence of analysis is as follows:

(1) GC/MS tuning with BFB. **[REQUIRED]**
(2) Analytical batch calibration standards (initial) or mid-range Continuing Calibration Standard (daily check of initial calibration), either of which could also be used to evaluate BFB for GC/MS tuning. [**REQUIRED**]
(3) Initial Calibration Verification. **[REQUIRED only after initial calibration]**
(4) Analytical batch LCS. **[REQUIRED]**
(5) Analytical batch LCSD. **[REQUIRED]**
(6) Analytical batch LMB. **[REQUIRED]**
(7) Batch samples (up to 12 hours).
(8) Matrix Duplicate. **[As requested by data user]**
(9) Matrix Spike/Matrix Spike Duplicate. **[As requested by data user]**

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

10.2 Minimum Instrument QC

10.2.1 **Peak Resolution**

The n-pentane (C_5) peak must be adequately resolved from any solvent front that may be present on the chromatogram. This is achievable using the recommended chromatographic columns and purge-and-trap procedures. Coelution of the m- and p- xylene isomers is permissible. All surrogates and internal standards 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 **Internal Standards**

The internal standard area counts in each field sample, LMB, LCS, and other QC samples must be evaluated. The internal standard area counts must be within 50-200% of the internal standard area counts in the corresponding Continuing Calibration Standard. If the internal standard area counts fall outside of this range, check calculations to locate possible errors, check the sample introduction system for leaks or other malfunctions, 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) The internal standard exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in the sample.

If a sample with an internal standard 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 internal standard recovery problems. This approach can be used as long as RLs less than or equal to 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 internal standards outside of the acceptable range after re-analysis must also be noted on the data report form and discussed in the laboratory narrative.

10.2.3 **Mass spectrometer tuning** must be performed daily (once every 12 hours) before any analyses are conducted. Acceptance criteria for the recommended tuning standard, BFB, are provided in Table 2.

10.2.4 **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.

10.2.5 **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 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.

10.2.6 **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 Section 9.3).

10.2.7 **Calibration**

10.2.7.1 **Initial Calibration:** RRFs 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 RRFs may be assumed if the %RSD over the working range of the calibration curve is ≤ 20 for Target VPH Analytes and ≤ 25 for hydrocarbon ranges. (See Section 9.4). For linear regression, r must be ≥ 0.99.

10.2.7.2 **Continuing Calibration Standard:** The Continuing Calibration Standard must be analyzed daily every 12 hours prior to sample analysis to verify the accuracy of the calibration of the instrument. For Target VPH Analytes and hydrocarbon ranges, the %D or Percent Drift must be ≤ 20. 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.

10.2.8 **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.

10.2.9 **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 10.2.8 for corrective actions associated with recoveries outside of acceptance limits.

10.2.10 **Surrogate Spike Recoveries**

10.2.10.1 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%. 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 18 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 18. 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 7.8). 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/MS 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

As per Section 9.4.3, calibrate the GC/MS as follows:

11.1.1 Calculate an average RRF or linear regression calibration curve for the Target VPH Analytes (benzene, toluene, ethylbenzene, m-, p-, and o-xylenes, naphthalene, and MTBE).

11.1.2 Calculate an average RRF for the surrogate standard.

11.1.3 Using total ion area counts as determined in Section 9.4.3.7, calculate an average collective RRF for the total concentration of the C_5 - C_8 Aliphatic Hydrocarbons. Tabulate the collective peak area response of the 6 components (n-pentane, n-hexane, cyclohexane, 2,3-dimethylpentane, n-heptane, n-octane) against the collective concentration injected.

11.1.4 Using total ion area counts as determined in Section 9.4.3.8, calculate an average collective RRF for the total concentration of C_9 - C_{12} Aliphatic Hydrocarbons. Tabulate the collective peak area response of the 6 components (2,3-dimethylheptane, n-nonane, n-decane, n-undecane, n-dodecane, butylcyclohexane) against the collective concentration injected.

11.1.5 Using the extracted ion area counts for m/z 120 and m/z 134 as determined in Section 9.4.3.9, calculate an average collective RRF for the total concentration of C_9 - C_{10} Aromatic Hydrocarbons. Tabulate the collective peak area response of the 5 components (isopropylbenzene, 1-methyl-3-ethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, p-isopropyltoluene) against the collective concentration injected.

11.2 Sample Analysis

11.2.1 Target VPH Analytes

11.2.1.1 Determine the peak area counts for the Target VPH Analytes using the primary (quantitation) ions.

11.2.1.2 Determine the peak area counts for the surrogate standard and internal standards using the primary (quantitation) ions.

11.2.1.3 Using the equations contained in Section 9.6, calculate the concentrations of the Target VPH Analytes and surrogate standard.

11.2.2 C_9-C_{10} Aromatics

11.2.2.1 Determine the total of extracted ion area counts for m/z 120 and m/z 134 for all peaks eluting 0.1 minutes after the Rt for o-Xylene and 0.1 minutes before the Rt for naphthalene.

11.2.2.2 Using the equations contained in Section 9.6, calculate the concentration of the C_9 through C_{10} Aromatic Hydrocarbons.

11.2.3 C_5-C_8 Aliphatics and C_9-C_{12} Aliphatics

11.2.3.1 Determine the total ion 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. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

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

11.2.3.3 Using the equations contained in Section 9.6, calculate the concentrations of C_5 through C_8 Aliphatic Hydrocarbons and C_9 through C_{12} Aliphatic Hydrocarbons.

11.2.4 Data Adjustments

11.2.4.1 By definition, the collective concentrations of aliphatic and aromatic hydrocarbon ranges 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 11.2.3, to eliminate "double counting" of analytes.

11.2.4.2 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.

11.2.4.2.1 Subtract the total area counts of the surrogate and internal standard compound(s) from the collective area count of any range in which they elute.

11.2.4.2.2 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").

11.2.4.2.3 Subtract the concentrations of the Target VPH Analytes from the appropriate aliphatic hydrocarbon 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).

11.2.4.3 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 by GC/MS Method data is presented in Appendix 2. 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/MS 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 2) precludes the affected data from achieving "Presumptive Certainty" status. If a significant modification to the VPH by GC/MS Method is utilized, an attachment to the analytical report must be included to demonstrate compliance with the method performance requirements of Section 1.11 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 2 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 other 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 other than a purge-and-trap sample preparation procedure.

11.3.1.2 The use of a heated purge.

11.3.1.3 The use of alternative detectors other than GC/MS to quantify Target VPH Analytes and/or hydrocarbon range concentrations.

11.3.1.4 The use of extracted ions other than m/z 120 and 134 to quantify C_9-C_{10} aromatic hydrocarbons.

11.3.1.5 The use of non-linear regression (i.e., quadratic equations) for the calibration of Target VPH Analytes and/or hydrocarbon ranges.

11.3.1.6 Failure to provide all of the data and information presented in Appendix 2 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).
- 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 internal standard or surrogate issues yields similar non-conformances, the laboratory must report results of both analyses.

(2) If reanalysis due to internal standard or surrogate issues is performed outside of holding time and yields acceptable internal standard or surrogate recoveries, the laboratory must report results of both analyses.

(3) If sample is not reanalyzed for internal standard or 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 Analytical Protocol Certification Form is included in Appendix 2 of this method.

11.4 Reporting Requirements for Non-VPH Compounds

As described in Section 9.6.2, the contribution (i.e., area count) of compounds not meeting the regulatory definition of the aromatic and/or aliphatic hydrocarbons, defined in Sections 3.5, 3.6 and 3.7, that elute within the method-defined retention time windows for these hydrocarbon ranges, may be excluded from collective hydrocarbon range concentrations **at the discretion of the data user,** providing the compound meets the requirements for positive **GC/MS identification** as described below.

- If the non-VPH compound co-elutes with an aliphatic petroleum hydrocarbon, the total ion area count may not be subtracted from the aliphatic range.

- In complex sample matrices (i.e., many co-eluting peaks, complex petroleum patterns), this type of data adjustment may not be possible.

All data adjustments and the presence of positively identified non-VPH compounds must be disclosed on the laboratory report form and laboratory narrative. If this data adjustment is requested by the data user, the laboratory should evaluate those peaks with a peak height ≥ ½ of the peak height of the closest internal standard. Refer to Table 9 for a list of common non-VPH compounds that elute within the aliphatic and aromatic hydrocarbon ranges.

Requirements for Positive GC/MS Identification of Non-VPH Compounds:

- Spectral identification must be evaluated by a qualified mass spectrometrist.
- The spectral library match must be ≥ 85% for an identification to be made.
- The major ions in the reference spectrum (i.e., ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or for the presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks.
- Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different chromatographic retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs (as a mixture of two isomers).

NOTE: The analyst may use professional judgment for the identification of non-VPH compounds. If non-VPH compounds are identified using criteria different than the criteria listed above, this should be disclosed in the laboratory narrative.

If the data user determines that the presence of the non-VPH compound reported by the laboratory may appreciably increase the overall risk posed by the site or the utility/cost of the potential remedial measures under consideration, additional analytical work may be requested to verify the identification and/or concentration of the reported non-VPH compound, either by reanalysis or resampling. This contingency will require additional coordination and communication between the laboratory and the data user.

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

An example VPH by GC/MS Method chromatogram is provided in Appendix 1. 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

(1) ASTM Method D2216-92, *Determination of Moisture Content of Soils and Sediments.*

(2) ENSR, 1999: *Laboratory Method Validation Study for the Determination of Volatile Petroleum Hydrocarbons in Indoor Air*, ENSR Corporation, June 1999.

(3) MassDEP, 1994: *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*, Massachusetts Department of Environmental Protection, August 1994.

(4) MassDEP, 1998: *Report on Results of the Fall 1997 VPH/EPH Round Robin Testing Program*, Massachusetts Department of Environmental Protection, January 12, 1998.

(5) 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.

(6) MassDEP, 2003: *Updated Petroleum Hydrocarbon Fraction Toxicity Values For VPH/EPH/APH Methodology*, Massachusetts Department of Environmental Protection, November 2003.

(7) MassDEP, 2004: *Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)*, Revision 1, Massachusetts Department of Environmental Protection, May 2004.

(8) MassDEP, 2009: *Method for the Determination of Air-Phase Petroleum Hydrocarbons (APH)*, Revision 1, Massachusetts Department of Environmental Protection, December 2009.

(9) MassDEP, 2016: *Evaluation of MassDEP Volatile Petroleum Hydrocarbon (VPH) Methods*, Massachusetts Department of Environmental Protection, June 2016.

(10) USEPA: *SW-846 Test Methods for Evaluating Solid Waste*, 3rd Edition; Methods 5030B, 5035A, 8000D, and 8260B.

TABLES

Table 1. VPH Component Standard

Compound	CAS Number	Boiling Point (°C)	Mol. Wt. (g/mol)	VPH Analysis Function	Retention Time (minutes)[1]	Retention Time (minutes)[2]
n-Pentane	109660	36	72.15	RC/RM	2.24	NP
Methyl tertiary butyl ether (MTBE)	1634044	55	88.15	TA	3.50	3.44
n-Hexane	110543	69	86.17	RC	3.65	NP
Benzene	71432	80	78.11	TA	6.17	6.73
Cyclohexane	110827	81	84.16	RC	5.55	6.03
2,3-Dimethylpentane	565593	90	100.20	RC	5.21	5.67
n-Heptane	142825	98	100.20	RC	5.92	NP
Toluene	108883	111	92.14	TA	9.06	9.61
n-Octane	111659	126	114.23	RC	8.63	9.32
Ethylbenzene	100414	136	106.17	TA	11.77	11.83
2,3-Dimethylheptane	3074713	141	128.26	RC	10.23	10.68
m-Xylene	108383	139	106.17	TA	11.91	11.93
p-Xylene	106423	138	106.17	TA	11.91	11.93
o-Xylene	95476	144	106.17	TA/RM	12.73	12.55
n-Nonane	111842	151	128.26	RC/RM	11.38	11.57
Isopropylbenzene	98828	152	120.20	RC	13.44	13.04
1-Methyl-3-ethylbenzene	620144	161	120.20	RC	14.42	13.66
1,3,5-Trimethylbenzene	108678	165	120.20	RC	14.53	13.74
n-Decane	124185	174	142.28	RC	13.99	13.43
1,2,4-Trimethylbenzene	95636	169	120.20	RC	16.08	14.70
p-Isopropyltoluene	99876	177	134.22	RC	15.81	14.53
Butylcyclohexane	1678939	181	140.27	RC	15.38	14.30
n-Undecane	1120214	196	156.32	RC	16.21	14.77
Naphthalene	91203	218	128.17	TA/RM	19.63	16.93
n-Dodecane	112403	216	170.33	RC	17.96	15.84
Internal Standards (IS)/Surrogate						
Fluorobenzene	462066	85	96.10	IS	6.47	NP
1,4-Difluorobenzene	540363	89	114.09	IS	NP	7.18
Chlorobenzene-d5	3114554	130	117.59	IS	11.60	11.67
1,4-Dichlorobenzene-d4	3855821	173	151.03	IS	16.08	14.70
Toluene-d8	2037265	110	100.19	Surrogate	8.93	9.49

[1] Results obtained using the VOCOL™ column and chromatographic conditions described in Sections 6.2.2 and 9.2, respectively.
[2] Results obtained using the RTX-502.2™ column and chromatographic conditions described in Section 6.2.2 and 9.2, respectively.
NP – Not provided during column evaluation.

TA- Target Analyte	**RC - Range Calibration Aliphatic**
RM - Range Marker	**RC - Range Calibration Aromatic**

Table 2. BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	15 to 40 percent of m/z 95
75	30 to 60 percent of m/z 95
95	Base peak, 100 percent relative abundance
96	5 to 9 percent of m/z 95
173	Less than 2 percent of m/z 174
174	Greater than 50 percent of m/z 95
175	5 to 9 percent of m/z 174
176	Greater than 95 percent but less than 101 percent of m/z 174
177	5 to 9 percent of m/z 176

Table 3a. Recommended VPH Calibration Standard Concentrations

Component	Nominal Concentration (µg/L)				
n-Pentane	1	5	25	100	200
Methyl tertiary butyl ether	1	5	25	100	200
n-Hexane	1	5	25	100	200
Benzene	1	5	25	100	200
Cyclohexane	1	5	25	100	200
2,3-Dimethylpentane	1	5	25	100	200
n-Heptane	1	5	25	100	200
Toluene	1	5	25	100	200
n-Octane	1	5	25	100	200
Ethylbenzene	1	5	25	100	200
2,3-Dimethylheptane	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
n-Nonane	1	5	25	100	200
Isopropylbenzene	1	5	25	100	200
1-Methyl-3-ethylbenzene	1	5	25	100	200
1,3,5-Trimethylbenzene	1	5	25	100	200
n-Decane	1	5	25	100	200
1,2,4-Trimethylbenzene	1	5	25	100	200
p-Isopropyltoluene	1	5	25	100	200
Butylcyclohexane	1	5	25	100	200
n-Undecane	1	5	25	100	200
Naphthalene	1	5	25	100	200
n-Dodecane	1	5	25	100	200

Table 3b. Initial Calibration of VPH Hydrocarbon Range Components

Hydrocarbon Range	Hydrocarbon Range Compounds Used to Establish Range Response 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	1	1	6
	n-Hexane	2	5	30
	Cyclohexane	3	25	150
	2,3-Dimethylpentane	4	100	600
	n-Heptane	5	200	1200
	n-Octane			
C_9-C_{12} Aliphatic	2,3-Dimethylheptane	1	1	6
	n-Nonane	2	5	30
	n-Decane	3	25	150
	n-Undecane	4	100	600
	n-Dodecane	5	200	1200
	Butylcyclohexane			
C_9-C_{10} Aromatic	Isopropylbenzene	1	1	5
	1-Methyl-3-ethylbenzene	2	5	25
	1,3,5-Trimethylbenzene	3	25	125
	1,2,4-Trimethylbenzene	4	100	500
	p-Isopropyltoluene	5	200	1000

Table 4. 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 0-6ºC	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 0-6ºC	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 0-6ºC	28 days

[1] Heated purge is considered a significant modification to the method, as per Section 11.3.1.
[2] Refer to Appendix 3 for details on sample collection or optional collection/storage devices.

Table 5. VPH Marker Compounds and Range Retention Time Windows

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

[1] The retention time for Dodecane (C_{12}) is approximately 1-2 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.

Table 6. 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 4. Heated purge is considered a significant modification to the method, as per Section 11.3.1.	

Table 7. Primary (Quantitation) & Secondary Ions for VPH Components/Internal Standards/Surrogates

VPH Components	CAS Number	Target VPH Analyte	Primary (Quantitation) Ion	Secondary Ion(s)
n-Pentane	109660		43	57, 72
Methyl tertiary butyl ether (MTBE)	1634044	✓	73	45
n-Hexane	110543		57	41, 43, 56
Cyclohexane	110827		56	84, 41
2,3-Dimethylpentane	565593		56	43, 57, 41
Benzene	71432	✓	78	52, 51
n-Heptane	142825		43	71, 57, 100
Toluene	108883	✓	91	92
n-Octane	111659		43	85, 57, 71
2,3-Dimethylheptane	3074713		43	84, 85
Ethylbenzene	100414	✓	91	106
m- & p-Xylene	1330207	✓	91	106, 105
n-Nonane	111842		43	57, 85
o-Xylene	95476	✓	91	106, 105
Isopropylbenzene	98828		105	120
1-Methyl-3-ethylbenzene	620144		105	120
1,3,5-Trimethylbenzene	108678		105	120
n-Decane	124185		57	43, 71, 85
Butylcyclohexane	1678939		83	55, 82
p-Isopropyltoluene	99876		119	105, 134
1,2,4-Trimethylbenzene	95636		105	120
n-Undecane	1120214		57	43, 71, 85
n-Dodecane	112403		57	43, 71, 85
Naphthalene	91203	✓	128	
Internal Standards/Surrogates				
Fluorobenzene (IS #1)	462066		96	70
1,4-Difluorobenzene (IS #1)	540363		114	63, 88
Toluene-d8 (Surrogate)	2037265		98	100, 42
Chlorobenzene-d5 (IS #2)	3114554		117	119, 82
1,4-Dichlorobenzene-d4 (IS #3)	3855821		152	115, 150

NOTE: All VPH Components are listed in Table 7 for reference purposes. Only the RRFs for Target VPH Analytes need to be determined on a compound-specific basis.

Table 8. Internal Standards and Associated Target VPH Analytes and Hydrocarbon Ranges

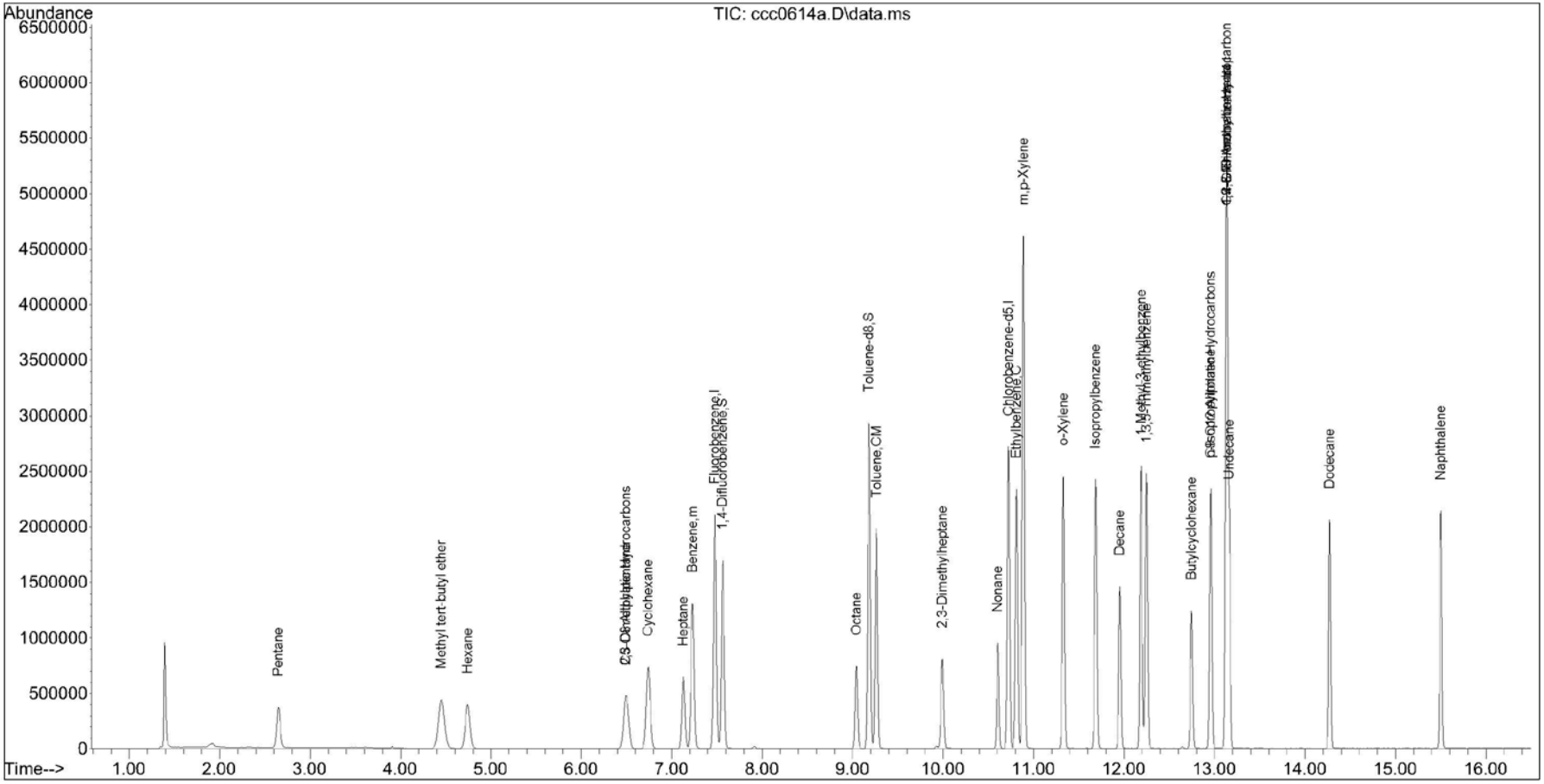
Fluorobenzene or 1,4-Difluorobenzene (IS #1)	Chlorobenzene-d5 (IS #2)	1,4-Dichlorobenzene-d4 (IS #3)
Methyl tertiary butyl ether (MTBE) Benzene C_5-C_8 Aliphatics	Ethylbenzene m- & p-Xylenes o-Xylene Toluene Toluene-d8	Naphthalene C_9-C_{12} Aliphatics C_9-C_{10} Aromatics

Table 9. List of Common Non-VPH Compounds That Elute Within the VPH Method Ranges

Hydrocarbon Range	Potential Non-VPH Compounds
C_5-C_8 Aliphatic Hydrocarbons	Acetone may co-elute/interfere with isopentane. Isopropyl alcohol, methyl ethyl ketone, trichloroethene, tetrachloroethene, tetrahydrofuran, hexanal, 1-butanol, hexamethylsiloxane
C_9-C_{12} Aliphatic Hydrocarbons	Terpenes (e.g., a-pinene, d-limonene), phenol, benzaldehyde, n-chain aldehydes, 2-ethyl-1-hexanol, siloxanes, dichlorobenzenes
C_9-C_{10} Aromatic Hydrocarbons	Siloxanes, a-pinene, and d-limonene may slightly interfere (contribute to the area of ions 120/134) if present at high concentrations.

APPENDIX 1

VPH BY GC/MS METHOD CHROMATOGRAM


Abundance
TIC: ccc0614a.D\data.ms
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
16.00
Pentane
Methyl tert-butyl ether
Hexane
Cyclohexane
Heptane
Benzene,m
Toluene-d8,S
Toluene,CM
Octane
2,3-Dimethylheptane
Nonane
Chlorobenzene-d5,I
Ethylbenzene,C
m,p-Xylene
o-Xylene
Isopropylbenzene
Decane
Butylcyclohexane
Undecane
Dodecane
Naphthalene

APPENDIX 2

REQUIRED VPH DATA REPORT INFORMATION

Exhibit 1 Required VPH Data Report Information

Exhibit 2 MassDEP Analytical Protocol Certification Form

APPENDIX 2
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 2
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 3

1. Collecting and Preserving VPH Soil/Sediment Samples

2. Collecting and Preserving VPH Aqueous Samples

APPENDIX 3
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: Pre-label each container with a unique alpha/numerical designation. Obtain and record tare (empty) 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.

APPENDIX 3
Collecting and Preserving VPH Soil/Sediment Samples

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 3
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 4

SHIPPING METHANOL-PRESERVED SAMPLES

APPENDIX 4
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 5

VPH BY GC/MS METHOD CALCULATIONS

APPENDIX 5
VPH by GC/MS Method Calculations

This Appendix provides (1) example calculations of RRFs for VPH aliphatic and aromatic hydrocarbon ranges and the target analyte Benzene based on multi-point calibration data and (2) example calculations of sample concentrations for VPH aliphatic and aromatic hydrocarbon ranges and the target analyte Benzene based on the calculated RRFs, simulated area counts, and other sample-specific data. The VPH by GC/MS Method Analytical Flow Chart is shown in Figure 5-1.

Example Calculations
Refer to information found on Tables 5-1 through 5-4.

Equation 1: Relative Response Factor for Target VPH Analytes
RRFs are calculated for each Target VPH Analyte using the area response of the analyte's primary (quantitation) ion, its true concentration, the area response of the associated internal standard's primary (quantitation) ion, and its concentration, using Equation 1 from the VPH by GC/MS Method.

RRF calculated for Benzene, Calibration Level 1, using data found in Tables 5-2 and 5-3:

$$RRF_{Benzene} = [(A_{EC}) * (C_I)]/[(A_{EI}) * (C_C)]$$

A_{EC} = 3556	area count of the primary quantitation ion for Benzene (m/z 78)
C_I = 50 µg/L	concentration of internal standard (IS1)
A_{EI} = 35531	area count of the primary quantitation ion for the associated internal standard (m/z 96)
C_C = 1 µg/L	concentration of Benzene, Calibration Level 1

$$RRF_{Benzene} = [(3556) * (50)]/[(35531) * (1)]$$
$$RRF_{Benzene} = 5.004$$

Equation 2: Relative Response Factor for C_5-C_8 Aliphatic Hydrocarbons
The RRF for the C_5-C_8 Aliphatic range is based on a correlation between the total concentration of aliphatic components eluting within this range (see Table 3b of the VPH by GC/MS method) and their total ion area counts, using Equation 2 from the VPH by GC/MS Method.

RRF calculated for C_5-C_8 Aliphatic Hydrocarbons, Calibration Level 1, using data found in Tables 5-2 and 5-3:

$$RRF_{Range_x} = [(A_T) * (C_I)]/[(A_{EI}) * (C_T)]$$

A_T = 18097	total ion area count of C_5-C_8 Aliphatic range (six aliphatic components)
C_I = 50 µg/L	concentration of internal standard (IS1)
A_{EI} = 35531	area count of the primary ion for the associated internal standard (m/z 96)
C_T = 6 µg/L	total concentration of C_5-C_8 Aliphatic range, Calibration Level 1 (six aliphatic components)

$$RRF_{Range} = [(18097) * (50)]/[(35531) * (6)]$$

$$RRF_{Range} = 4.244$$

APPENDIX 5
VPH by GC/MS Method Calculations

Equation 3: Relative Response Factor for C_9-C_{12} Aliphatic Hydrocarbons

The RRF for the C_9-C_{12} Aliphatic range is based on a correlation between the total concentration of aliphatic components eluting within this range (see Table 3b of the method) and their total ion area counts, using Equation 3 from the VPH by GC/MS Method.

RRF calculated for C_9-C_{12} Aliphatic Hydrocarbons, Calibration Level 1, using data found in Tables 5-2 and 5-3:

$$RRF_{Range_x} = [(A_T) * (C_I)] / [(A_{EI}) * (C_T)]$$

A_T = 32296	total ion area count of C_9-C_{12} Aliphatic range (six aliphatic components)
C_I = 50 ug/L	concentration of internal standard (IS3)
A_{EI} = 316020	area count of the primary ion for the associated internal standard (m/z 152)
C_T = 6 ug/L	total concentration of C_9-C_{12} Aliphatic range, Calibration Level 1 (six aliphatic components)

$$RRF_{Range} = [(32296) * (50)] / [(316020) * (6)]$$

$$RRF_{Range} = 0.8516$$

Equation 4: Relative Response Factor for C_9-C_{10} Aromatic Hydrocarbons

The RRF for the C_9-C_{10} Aromatic range is calculated using the total concentration of aromatic components eluting within this range (see Table 3b of the VPH by GC/MS Method) and a summation of the m/z 120 and m/z 134 extracted ion area counts for the aromatic components eluting within this range, using Equation 4 from the VPH by GC/MS Method

RRF calculated for C_9-C_{10} Aromatic Hydrocarbons, Calibration Level 1, using data found in Tables 5-2 and 5-3:

$$RRF_{Range_x} = [(A_T) * (C_I)] / [(A_{EI}) * (C_T)]$$

A_T = 54343	summation of extracted ion area counts (m/z 120 + m/z 134: five aromatic components)
C_I = 50 ug/L	concentration of internal standard (IS3)
A_{EI} = 316020	area count of the primary ion for the associated internal standard (m/z 152)
C_T = 5 ug/L	total concentration of C_9-C_{10} Aromatic range, Calibration Level 1 (five aromatic components)

$$RRF_{Range} = [(54343) * (50)] / [(316020) * (5)]$$

$$RRF_{Range} = 1.720$$

APPENDIX 5
VPH by GC/MS Method Calculations

Equation 5: Percent Relative Standard Deviation
For each target compound and hydrocarbon range a percent relative standard deviation (%RSD) is calculated from the RRFs generated for each point of the curve using Equation 5 from the VPH by GC/MS Method.

Example: Benzene from Table 5-1:

Compound	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Mean	SD
Benzene	5.004	4.713	4.826	4.097	4.147	4.557	0.4113

$$\%RSD_{Benzene} = [(SD_{n-1})/(AVGx)]*100]$$

%RSD =	percent relative standard deviation
SD_{n-1} = 0.4113	standard deviation (n-1 degrees of freedom)
AVG_x = 4.557	mean response factor from the initial calibration

$$\%RSD_{Benzene} = (0.4113/4.557)*100$$
$$\%RSD_{Benzene} = 9.0$$

Equation 7: Percent Difference
Calculate a percent difference for Benzene in a continuing calibration standard having a calculated RRF of 4.769 using Equation 7 from the VPH by GC/MS Method:

$$\%D_{Benzene} = [(RRF_C) - (RRF_I)]/[(RRF_I)]*100$$

%D =	percent difference
RF_C = 4.769	response factor from the continuing calibration
RF_I = 4.557	mean response factor from the initial calibration

$$\%D_{Benzene} = [(4.769) - (4.557)]/[(4.557)]*100$$
$$\%D_{Benzene} = 4.6$$

Equation 8: Calculation of Sample Results in µg/L: Target Analyte (Benzene)
Calculate a final µg/L concentration for Benzene using data found in Table 5-4 and Equation 8 from the VPH by GC/MS Method:

$$\mu g/L_{Benzene} = [(A_x)*(C_{IS})]/[(A_{IS})*(RRF_{avg})]*DF$$

A_x = 60285	area count of the primary ion for Benzene (m/z 78)
C_{IS} = 50 µg/L	concentration of internal standard (IS1)
A_{IS} = 31534	area count of the primary ion for the associated internal standard (m/z 96)
RRF_{avg} = 4.557	average RRF for benzene
DF = 1.0	dilution factor

$$\mu g/L_{Benzene} = [(60285)*(50)]/[31534)*(4.557)]*1.0$$
$$\mu g/L_{Benzene} = 21.0$$

APPENDIX 5
VPH by GC/MS Method Calculations

Equation 10: Calculation of Sample Results in µg/L: C_5-C_8 Aliphatic Range

A. Calculate a preliminary (unadjusted) µg/L concentration for C_5-C_8 Aliphatic range using data found in Table 5-4 and Equation 10 from the VPH by GC/MS Method:

$$\mu g / L_{Aliphatic} = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})] * DF$$

A_x =	823563	total ion area count of all peaks eluting within this range (excluding internal standard and surrogate areas)
C_{IS} =	50 µg/L	concentration of internal standard (IS1)
A_{IS} =	31534	area count of the primary ion for the associated internal standard (m/z 96)
RRF_{avg} =	3.744	average RRF for C_5-C_8 Aliphatic range
DF=	1.0	dilution factor

$$\mu g / L_{Aliphatic} = [(823563) * (50)] / [(31534) * (3.744)] * 1.0$$
$$\mu g / L_{Aliphatic} = 349$$

B. Calculate a final µg/L concentration for C_5-C_8 Aliphatic range using data found in Table 5-4:

Final C_5-C_8 Aliphatic range µg/L concentration = (Preliminary µg/L concentration) – (concentrations of Target VPH Analytes which elute within the C_5-C_8 Aliphatic range)

Final C_5-C_8 Aliphatic range µg/L concentration = (349 µg/L) – (concentrations of MTBE, benzene, toluene)

Final C_5-C_8 Aliphatic range µg/L concentration = (349 µg/L) – (30.8 + 21.0 + 21.4 µg/L)

Final C_5-C_8 Aliphatic range µg/L concentration = 275.8 µg/L

Equation 12: Calculation of Sample Results in µg/L: C_9-C_{10} Aromatic Range

Calculate a final µg/L concentration for C_9-C_{10} Aromatic range using data found in Table 5-4 and Equation 12 from the VPH by GC/MS Method:

$$\mu g / L_{Aromatic} = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})] * DF$$

A_x =	3217570	summation of extracted ion area counts (m/z 120 + m/z 134) eluting within range
C_{IS} =	50 µg/L	concentration of internal standard (IS3)
A_{IS} =	317012	area count of the primary ion for the associated internal standard (m/z 152)
RRF_{avg} =	1.568	average RRF for C_9-C_{10} Aromatic range
DF=	1.0	dilution factor

$$ug / L_{Aromatic} = [(3217570) * (50)] / [(317012) * (1.568)] * 1.0$$
$$ug / L_{Aromatic} = 324$$

APPENDIX 5
VPH by GC/MS Method Calculations

Equation 13: Calculation of Samples Results in µg/L: C_9-C_{12} Aliphatic Range

A. Calculate a preliminary (unadjusted) µg/L concentration for C_9-C_{12} Aliphatic range using data found in Table 5-4 and Equation 13 from the VPH by GC/MS Method:

$$\mu g / L_{Aliphatic} = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})] * DF$$

A_x =	5783146	total ion area count of all peaks eluting within this range (excluding internal standards)
C_{IS} =	50 µg/L	concentration of internal standard (IS3)
A_{IS} =	317012	area count of the primary ion for the associated internal standard (m/z 152)
RRF_{avg} =	0.8126	average RRF for C_9-C_{12} Aliphatic range
DF=	1.0	dilution factor

$$\mu g / L_{Aliphatic} = [(5783146) * (50)] / [(317012) * (0.8126)] * 1.0$$
$$\mu g / L_{Aliphatic} = 1122$$

B. Calculate a final µg/L concentration for C_9-C_{12} Aliphatic range using data found in Table 5-4:

Final C_9-C_{12} Aliphatic range µg/L concentration = (Preliminary µg/L concentration) – (concentrations of ethylbenzene, m- & p-xylenes, o-xylene and C_9-C_{10} Aromatics)

Final C_9-C_{12} Aliphatic range µg/L concentration = (1122 µg/L) – (21.2 + 42.1 + 21.1 + 324 µg/L)

Final C_9-C_{12} Aliphatic range µg/L concentration = 713.6 µg/L

Equation 6: Percent Recovery

From information found in Table 5-4, calculate a percent recovery for Benzene having a true or spiked concentration of 25 µg/L.

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

%R =		percent recovery
C_{found} =	21.0	concentration of the analyte or range (µg/L)
C_{true} =	25	true concentration of the analyte or range (µg/L)

$$\%R_{Benzene} = [(21.0) / (25)] * 100$$
$$\%R_{Benzene} = 84$$

APPENDIX 5
VPH by GC/MS Method Calculations

Table 5-1: Relative Response Factors

Compound	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Mean	%RSD
Fluorobenzene (IS1)							
Methyl tertiary butyl ether (MTBE)	9.4945	8.9428	7.8004	7.7727	7.8686	8.3758	9.5
Benzene	5.0041	4.7133	4.8262	4.0966	4.1471	4.5575	9.0
Chlorobenzene-d5 (IS2)							
Toluene	2.1238	1.9733	1.9090	1.7850	1.6640	1.8910	9.3
Ethylbenzene	5.7562	5.3481	5.1738	5.2452	4.5100	5.2067	8.6
Xylene (m, p)	4.5629	4.8576	4.1012	3.8348	3.5750	4.1863	12.5
Xylene (o)	4.5280	4.2070	4.0698	3.8055	3.5477	4.0316	9.3
Toluene-d8	2.3857	2.3412	2.4699	2.3009	2.2989	2.3593	3.0
1,4-Dichlorobenzene-d4 (IS3)							
Naphthalene	1.1142	1.0538	1.0892	1.0686	1.0787	1.0809	2.1
C_5-C_8 Aliphatic Hydrocarbons	4.2444	3.9978	3.4871	3.4747	3.5176	3.7443	9.5
C_9-C_{12} Aliphatic Hydrocarbons	0.8516	0.8055	0.8325	0.8168	0.7565	0.8126	4.4
C_9-C_{10} Aromatic Hydrocarbons	1.7196	1.6264	1.3156	1.6492	1.5275	1.5677	10.0

APPENDIX 5
VPH by GC/MS Method Calculations

Table 5-2: Initial Calibration Curve Area Counts

Compound	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5
Fluorobenzene (IS1)	35531	36214	39788	41232	40515
n-Pentane	2223	10670	51129	211185	420147
Methyl tertiary butyl ether (MTBE)	6747	32386	155181	640965	1275183
n-Hexane	1391	6677	31993	132145	262899
Benzene	3556	17069	96012	337820	672084
Chlorobenzene-d5 (IS2)	143419	148189	146799	162114	172980
Cyclohexane	1788	8582	41124	169860	337932
2,3-Dimethylpentane	2999	14395	68977	284905	566811
n-Heptane	1827	8770	42021	173565	345303
Toluene	6092	29242	140116	578740	1151388
n-Octane	7869	37771	180987	747555	1487241
1,4-Dichlorobenzene-d4 (IS3)	316020	320770	297404	313031	336207
Ethylbenzene	16511	79253	379753	1700633	3120579
2,3-Dimethylheptane	9786	46973	225078	929670	1849554
Xylene (m, p)	26176	143968	602048	2486720	4947264
Xylene (o)	12988	62342	298724	1233860	2454732
n-Nonane	6763	32462	155549	642485	1278207
Toluene-d8	342161	346944	362579	373001	397666
Isopropylbenzene	12267	58882	282141	1165365	2318463
1-Methyl-3-ethylbenzene	10155	48744	233565	964725	1919295
1,3,5-Trimethylbenzene	9935	47688	228505	943825	1877715
n-Decane	4417	21202	101591	419615	834813
1,2,4-Trimethylbenzene	9383	45038	215809	891385	1773387
4-Isopropyltoluene	9002	43210	207046	855190	1701378
Butylcyclohexane	4510	21648	103730	428450	852390
n-Undecane	3083	14798	70909	292885	582687
Naphthalene	7042	33802	161966	668990	1450652
n-Dodecane	3737	17938	85951	355015	706293
C_5-C_8 Aliphatic Hydrocarbons	18097	86866	416231	1719215	3420333
C_9-C_{12} Aliphatic Hydrocarbons	32296	155021	742808	3068120	6103944
C_9-C_{10} Aromatics (m/z 120)	45341	217637	816138	4307395	8569449
C_9-C_{10} Aromatics (m/z 134)	9002	43210	162036	855190	1701378
C_9-C_{10} Aromatic Hydrocarbons	54343	260846	978174	5162585	10270827

APPENDIX 5
VPH by GC/MS Method Calculations

Table 5-3: Initial Calibration Standard Concentrations (µg/L)

Compound	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5
n-Pentane	1	5	25	100	200
Methyl tertiary butyl ether (MTBE)	1	5	25	100	200
n-Hexane	1	5	25	100	200
Benzene	1	5	25	100	200
Fluorobenzene (IS2)	50	50	50	50	50
Cyclohexane	1	5	25	100	200
2,3-Dimethylpentane	1	5	25	100	200
n-Heptane	1	5	25	100	200
Chlorobenzene-d5 (IS2)	50	50	50	50	50
Toluene	1	5	25	100	200
n-Octane	1	5	25	100	200
Ethylbenzene	1	5	25	100	200
2,3-Dimethylheptane	1	5	25	100	200
Xylene (m, p)	2	10	50	200	400
Xylene (o)	1	5	25	100	200
n-Nonane	1	5	25	100	200
Toluene-d8	50	50	50	50	50
1,4-Dichlorobenzene-d4 (IS3)	50	50	50	50	50
Isopropylbenzene	1	5	25	100	200
1-Methyl-3-ethylbenzene	1	5	25	100	200
1,3,5-Trimethylbenzene	1	5	25	100	200
n-Decane	1	5	25	100	200
1,2,4-Trimethylbenzene	1	5	25	100	200
4-Isopropyltoluene	1	5	25	100	200
Butylcyclohexane	1	5	25	100	200
n-Undecane	1	5	25	100	200
Naphthalene	1	5	25	100	200
n-Dodecane	1	5	25	100	200
C_5-C_8 Aliphatic Hydrocarbons	6	30	150	600	1200
C_9-C_{12} Aliphatic Hydrocarbons	6	30	150	600	1200
C_9-C_{10} Aromatics (m/z 120)	5	25	125	500	1000
C_9-C_{10} Aromatics (m/z 134)	5	25	125	500	1000
C_9-C_{10} Aromatic Hydrocarbons	5	25	125	500	1000

APPENDIX 5
VPH by GC/MS Method Calculations

Table 5-4: Sample Analysis Data

Compound	RT	Area	ISTD ug/L	Concentration ug/L
Fluorobenzene (IS1)	6.47	31534	50	
Methyl tertiary butyl ether (MTBE)	3.50	162682		30.8
Benzene	6.17	60285		21.0
Chlorobenzene-d5 (IS2)	11.60	147321	50	
Toluene	9.06	119314		21.4
Ethylbenzene	11.77	325648		21.2
Xylene (m, p)	11.91	518803		42.1
Xylene (o)	12.73	250488		21.1
Toluene-d8	8.93	357146		51.4
1,4-Dichlorobenzene-d4 (IS3)	16.08	317012	50	
Naphthalene	19.63	99759		14.6
C_5-C_8 Aliphatic Hydrocarbons - Unadjusted		823563[3]		349
C_5-C_8 Aliphatic Hydrocarbons[1]				276
C_9-C_{12} Aliphatic Hydrocarbons - Unadjusted		5783146[4]		1122
C_9-C_{12} Aliphatic Hydrocarbons[2]				714
C_9-C_{10} Aromatics (m/z 120)		2256810		
C_9-C_{10} Aromatics (m/z 134)		960760		
C_9-C_{10} Aromatic Hydrocarbons		3217570		324

[1]Excludes concentrations of MTBE, Benzene and Toluene.
[2]Excludes concentrations of ethylbenzene, m- & p-xylenes, o-xylene, and C_9-C_{10} aromatic hydrocarbons.
[3]Excludes total ion area counts of IS 1 and toluene-d_8.
[4]Excludes total ion area counts of IS 2 and IS 3.

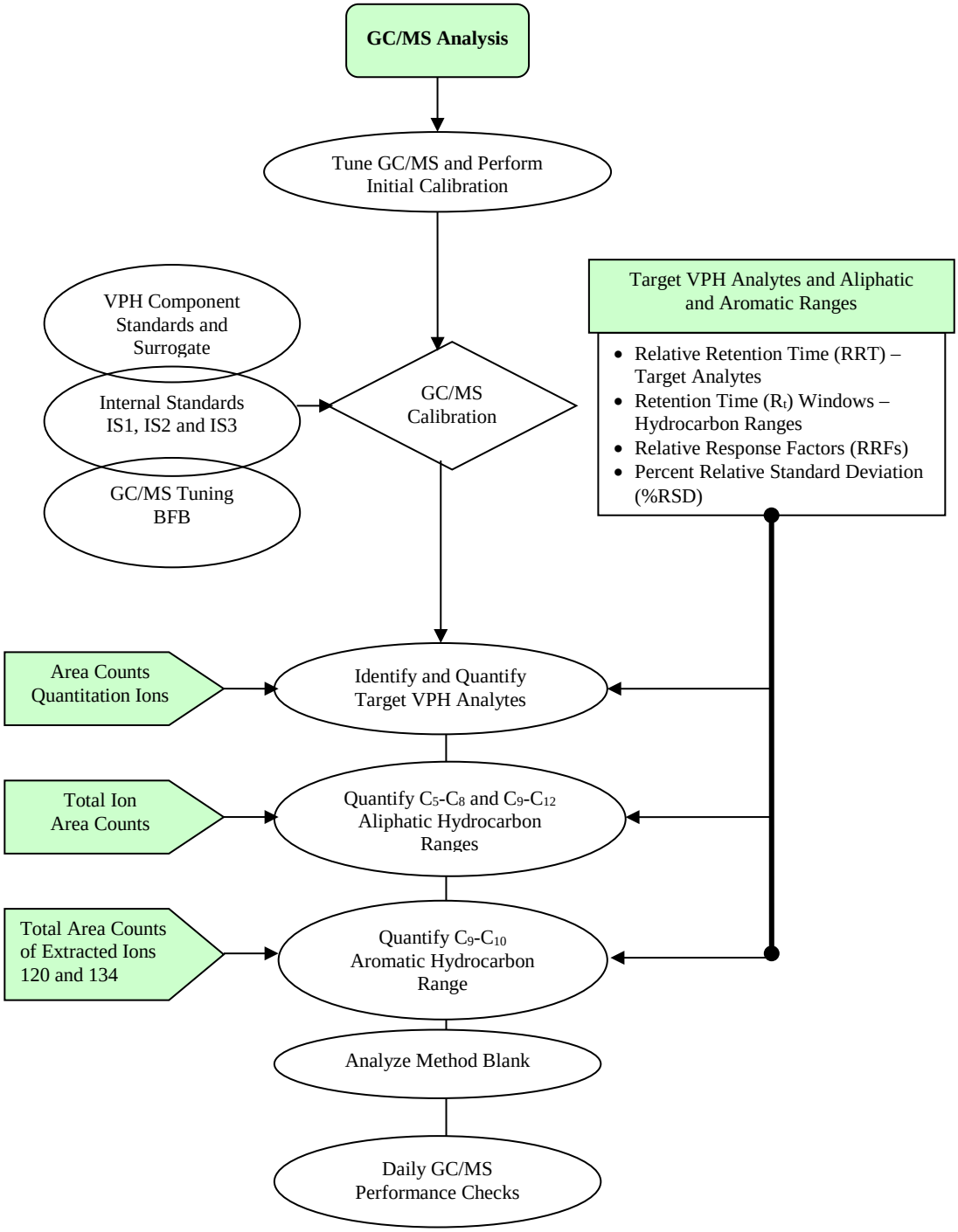
From Table 5 of Method. VPH Marker Compounds and Range Retention Time Windows

C_5-C_8 Aliphatic Hydrocarbons	0.1 min. before n-pentane	0.01 min. before n-nonane
C_9-C_{12} Aliphatic Hydrocarbons	0.01 min. before n-nonane	0.1 min. before naphthalene
C_9-C_{10} Aromatic Hydrocarbons	0.1 min. after o-xylene	0.1 min. before naphthalene

Ranges for Sample Data	Range Start RT	Range End RT
C_5-C_8 Aliphatic Hydrocarbons	2.14	12.72
C_9-C_{12} Aliphatic Hydrocarbons	12.72	19.53
C_9-C_{10} Aromatic Hydrocarbons	12.83	19.53

APPENDIX 5
VPH by GC/MS Method Calculations

Figure 5-1: VPH by GC/MS Method Analytical Flow Chart



APPENDIX 6

VPH by GC/MS METHOD CALIBRATION AND ANALYSIS USING LINEAR REGRESSON

APPENDIX 6
VPH by GC/MS 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 3a and 3b at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 9.4. 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 response ratios (area of Target VPH Analyte / area of internal standard) against the concentration ratio (concentration of the Target VPH Analyte/concentration of internal standard). 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 $\geq$ 0.99.

   Equation 6-1: Linear Regression: Target VPH Analytes

$$\frac{A_s \ C_{IS}}{A_{IS}} = aC_S + b$$

   where:

   a = the calculated slope of the line
   b = the calculated y intercept of the "best fit" line
   C_S = Concentration of the Target VPH Analyte (µg/L)
   A_S = Area count of the primary (quantitation) ion for the analyte of interest
   C_{IS} = Concentration of associated internal standard (µg/L)
   A_{IS} = Area count of the primary (quantitation ion) for the associated internal standard

   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 total ion integration and sum of the individual peak areas of the VPH components within each hydrocarbon range. Calculate the calibration curve for the C_9-C_{10} Aromatic Hydrocarbons using the sum of the 120 and 134 extracted ion chromatograms within the designated window for the hydrocarbon range. Tabulate the ratio of the summation of the peak areas to the area of the internal standard of all components in that hydrocarbon range (i.e., C_5-C_8 Aliphatic Hydrocarbons, 6 components) against the ratio of the total concentration of the hydrocarbon range to the concentration of the internal standard. 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 be $\geq$ 0.99.

   Note: Do not include the area of internal standards and surrogates when determining the calibration curve for C_9-C_{12} Aliphatic Hydrocarbons and C_5-C_8 Aliphatic Hydrocarbons.

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

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

$$\frac{A_T\ C_{IS}}{A_{IS}} = aC_T + b$$

where:

a = the calculated slope of the line
b = the calculated y intercept of the "best fit" line
C_T = summation of the concentrations (µg/L) of the six aliphatic VPH components which elute within this range for C_5-C_8 or C_9-C_{12} Aliphatic Hydrocarbons or summation of the concentrations of the five VPH components which elute within this range for C_9-C_{10} Aromatic Hydrocarbons
A_T = total ion area of the six aliphatic VPH components which elute within this range for C_5-C_8 or C_9-C_{12} Aliphatic Hydrocarbons or summation of areas of the extracted ions 120 and 134 for five aromatic VPH components which elute within this range for C_9-C_{10} Aromatic Hydrocarbons

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 Analyte and Hydrocarbon Range Concentrations using Linear Regression

$$\left(\frac{A_X\ C_{IS}}{A_{IS}} - b \right) \div a \times D = Conc.\ Analyte\ or\ HC\ Range\ (\mu g / L)$$

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

Conversion of µg/L to µg/kg
To convert target analyte or hydrocarbon range results from µg/L into µg/kg, use Equations 9 and 11 in the VPH by GC/MS method.

3. At a minimum, the working calibration curve must be verified every 12 hours prior to the analysis of samples to verify instrument performance and linearity. If the Percent Drift (% Drift), as determined by Equation 6-4, varies from the predicted response by more than ±20 for more than one Target VPH Analyte or hydrocarbon range, the instrument must be recalibrated.

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/MS 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)

APPENDIX 7
Initial Demonstration of Laboratory Capability (IDLC) for the MassDEP VPH by GC/MS Method

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/MS 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 8, 10, 12, and 13 in Section 9.6 of the VPH by GC/MS 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.

APPENDIX 7
Initial Demonstration of Laboratory Capability (IDLC) for MassDEP VPH by GC/MS Method

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 10.2.8 of the VPH by GC/MS 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.

APPENDIX 7
Initial Demonstration of Laboratory Capability (IDLC) for MassDEP VPH by GC/MS Method

5.0 Method Detection Limit (MDL)

The determination of the MDL for the MassDEP VPH by GC/MS 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/MS Method do not approach (are considerably higher than) the sensitivity limits of the VPH by GC/MS 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/MS 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/MS 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)

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

$S_{x,n-1}$ = 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.

RRF_x = Representative RRF 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 RRF (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

APPENDIX 7
Initial Demonstration of Laboratory Capability (IDLC) for MassDEP VPH by GC/MS Method

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).