METHOD FOR THE DETERMINATION OF

EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)

Massachusetts Department of Environmental Protection

Bureau of Waste Site Cleanup

Commonwealth of Massachusetts

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Important Notice!

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

Peak Integration Techniques:

- For individual Target PAH Analytes, the peaks from the FID or GC/MS are individually integrated (valley to valley). This applies to samples and standards.
- For the collective ranges of aliphatic hydrocarbons (i.e., C_9-C_{18} and C_{19}-C_{36}), the chromatogram from the FID or GC/MS is continuously integrated (to baseline) between specified range "marker" compounds (e.g., n-nonane to n-nonadecane for C_9-C_{18} aliphatic hydrocarbons). This applies to samples only; see Calibration Approach for peak integration techniques associated with calibration standards.
- For the collective range of C_{11}-C_{22} Aromatic Hydrocarbons, the chromatogram from the FID or GC/MS is continuously integrated (to baseline) between specified range "marker" compounds (i.e., naphthalene to benzo[g,h,i]perylene). This applies to samples only; see Calibration Approach for peak integration techniques associated with calibration standards.
- For the surrogate standard, the peak is individually integrated (valley-to-valley), so that the area can be subtracted from the collective areas of the hydrocarbon ranges discussed above.

  NOTE: GC/MS analysis is only allowed on fractionated extracts and may not be used as a substitute for fractionation.

Calibration Approach:

- The calibration factors (CFs) for the aliphatic and aromatic hydrocarbon ranges are based on the correlation of collective FID or GC/MS area counts to the collective concentration values of a specified mixture of aliphatic and aromatic hydrocarbon standards, in which the collective FID or GC/MS area count is determined via the summation of individual valley-to-valley 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 FID or GC/MS chromatogram). This is necessary to ensure a conservative bias (i.e., an integration-to-baseline approach for the calibration standards would incorporate baseline "noise" which could lead to inappropriately elevated CF values resulting in inappropriately lower sample concentration levels which would not be health-protective).

Data Adjustments:

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

- When determining the collective area count for a specified hydrocarbon range (i.e., C_9-C_{18} or C_{19}-C_{36} Aliphatic Hydrocarbons or C_{11}-C_{22} Aromatic Hydrocarbons), it is necessary to subtract the individual (valley-to-valley) peak area of any surrogate standards that elute within that range, if applicable.
- The individual concentrations of the Target PAH Analytes must be subtracted from the C_{11}-C_{22} Aromatic Hydrocarbon concentration.

Updates/Changes in Method Revision 2.1

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

Technical Revisions:

- Section 7.5: More flexibility was added for the volume of surrogate to be added to aqueous and solid samples.
- Section 8.2: The timeframe for freezing soil/sediment samples was changed from 48 hours to 24 hours from the time of sampling.
- Section 9.7.2.14: A requirement from the existing EPH CAM Protocol was added regarding the evaluation of the low standard when linear regression is used. This is a new requirement to the method but existed in the CAM Protocol.
- Sections 9.7.2.16 and 10.2.2:
    - A requirement from the existing EPH CAM Protocol was added regarding the analysis of an ICV. This is a new requirement to the method but existed in the CAM Protocol.
    - The ICV acceptance criterion of 70-130% for each Target PAH Analyte and hydrocarbon range from the existing EPH CAM Protocol was added.
- Section 9.10.3 and Table 7: Details were added regarding how to evaluate naphthalene and 2-methylnaphthalene in aliphatic extracts analyzed by GC/MS with the associated corrective actions.
- Section 10.2.7: Details were added regarding appropriate corrective actions when the LCS recoveries are outside of the acceptance criteria.
- Section 10.3.1: Details were added regarding appropriate corrective actions when the matrix duplicate RPDs are outside of the acceptance criteria.
- Section 11.3.1.1.6: A new significant modification was added regarding the use of non-linear regression during calibration.
- Table 4: For soil/sediment samples which are frozen, the holding time was changed to require extraction within 14 days of thawing. The footnote in this table was also revised to indicate samples must be frozen within 24 hours from the time of sampling.

Clarifications:

- "Important Notice" added at the beginning of the method to clarify proper peak integration during calibration and sample quantitation and data adjustment steps during sample quantitation.
- Sections 9.7.2.8 – 9.7.2.10: clarified that individual peak areas should be utilized for integration during calibration of the hydrocarbon ranges.
- Section 9.9.2: More details were added regarding the quantitation of the hydrocarbon ranges in samples.
- Section 9.10: Clarification was provided to note that Target PAH Analytes may be quantified from a fractionated or unfractionated extract using GC/MS but aliphatic and aromatic hydrocarbon ranges can only be quantified from a fractionated extract if GC/MS is used.
- Section 10.2.7: Clarification was provided to note that the recoveries of hydrocarbon ranges (not individual aliphatic hydrocarbons) need to be evaluated in the LCS.
- Section 10.3.2: Clarification was provided to note that the recoveries of hydrocarbon ranges (not individual aliphatic hydrocarbons) need to be evaluated in the MS/MSD.
- Section 11.3.2: Clarification on reporting of re-analyses and dilutions was added.
- Appendix 3: MassDEP Analytical Protocol Certification Form was updated to most current version.

LIST OF ACRONYMS

ASTM	American Society for Testing and Materials
CAM	Compendium of Analytical Methods
CCV	Continuing Calibration Verification
CF	Calibration Factor
COD	1-Chlorooctadecane
%D	Percent Difference
DF	Dilution Factor
EPH	Extractable Petroleum Hydrocarbons
FID	Flame Ionization Detector
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
HCl	Hydrochloric Acid
HPLC	High Performance Liquid Chromatography
ICV	Initial Calibration Verification
I.D.	Internal Diameter
IDLC	Initial Demonstration of Laboratory Capability
IS	Internal Standard
K-D	Kuderna-Danish
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
LMB	Laboratory Method Blank
MassDEP	Massachusetts Department of Environmental Protection
MCP	Massachusetts Contingency Plan
MDL	Method Detection Limit
NAPL	Non-aqueous Phase Liquids
OSHA	Occupational Safety & Health Administration
OTP	ortho-Terphenyl
PAH	Polynuclear Aromatic Hydrocarbons
QC	Quality Control
%R	Percent Recovery
r	Correlation Coefficient
RL	Reporting Limit
RPD	Relative Percent Difference
%RSD	Percent Relative Standard Deviation
Rt	Retention Time
SIM	Selective Ion Monitoring
SOP	Standard Operating Procedure
SPE	Solid-Phase Extraction
SSB	System Solvent Blank
TPH	Total Petroleum Hydrocarbons

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

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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.

METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)

MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION (MassDEP)

1.0 SCOPE AND APPLICATION

1.1 This method is designed to measure the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in aqueous and soil/sediment matrices. Extractable aliphatic hydrocarbons are collectively quantitated within two carbon number ranges: C_9 through C_{18} and C_{19} through C_{36}. Extractable aromatic hydrocarbons are collectively quantitated within the C_{11} through C_{22} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150 °C (n-nonane) and 500 °C (benzo[g,h,i]perylene).

1.2 This method is based on a solvent extraction, silica gel solid-phase extraction (SPE)/fractionation process, and gas chromatography (GC) analysis using a flame ionization detector (FID). Note that gas chromatography/mass spectrometry (GC/MS) analysis is only allowed on fractionated extracts and may not be used as a substitute for fractionation. This procedure should be used by, or under the direct supervision of, analysts experienced in extractable organics analysis. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

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

1.4 In addition to the quantification of aliphatic and aromatic hydrocarbon ranges, the MassDEP EPH method is also designed to quantify the individual concentrations of Target Polynuclear Aromatic Hydrocarbon (PAH) Analytes, including Diesel PAH Analytes, in aqueous and soil/sediment matrices. Use of this method to identify and quantify these Target PAH analytes is optional. The Reporting Limits (RLs) for some of these PAHs in aqueous samples are greater than the notification and/or cleanup standards specified in the MCP for sites located in groundwater resource areas categorized as RCGW-1 in 310 CMR 40.0362(1)(a). In cases where it is necessary to demonstrate compliance with these criteria, the use of a GC/MS method in the selective ion monitoring (SIM) mode and/or a high performance liquid chromatography (HPLC) method may be necessary.

1.5 The fractionation step described in this method can be eliminated to allow for a determination of Total Petroleum Hydrocarbons (TPH), and/or to obtain qualitative "fingerprinting" information. While TPH provides little information on the chemical constituents, toxicity, or environmental fate of petroleum mixtures, it may be a cost-effective screening tool in cases where relatively low concentrations of contamination are suspected.

1.6 Petroleum products suitable for evaluation by this method include kerosene, fuel oil #2, fuel oil #4, fuel oil #6, diesel fuel, jet fuels, and certain lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, or other petroleum products which contain a significant percentage of hydrocarbons lighter than C_9 or with boiling points <150 °C. This method, in and of itself, is also not suitable for the evaluation of petroleum products which contain a significant percentage of hydrocarbons heavier than C_{36} or with boiling points >500 °C.

1.7 The RL of this method for each of the Target PAH 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 0.2 to 1.0 mg/kg in soil/sediment matrices, and 2 to 5 µg/L in aqueous matrices. The RLs for the collective hydrocarbon ranges are approximately 10 mg/kg in soil/sediment matrices, and approximately 100 µg/L in aqueous matrices. The RL for TPH is approximately 10 mg/kg in soil/sediment matrices and approximately 100 µg/L in aqueous matrices.

1.8 This method includes a data adjustment step to subtract the concentration of Target PAH Analytes from the concentration of C_{11} through C_{22} aromatic hydrocarbons. This data adjustment step may be taken by the laboratory or by the data user .

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

1.10 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of Target PAH Analytes, in that non-targeted hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantified as a Target or Diesel PAH Analyte. In addition, this method is subject to a "false negative" bias in the reporting of Target PAH Analytes, in that the ability to identify Target PAH Analytes at low concentrations may be inhibited if a large unresolved complex mixture is present. While cleanup procedures specified in this method to segregate aliphatic and aromatic ranges will serve to mitigate these concerns, confirmatory analysis by dissimilar columns, GC/MS analysis, or other suitable method is recommended in cases where a Target PAH Analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where co-elution of a non-targeted hydrocarbon compound is suspected.

1.11 The first draft of this method was evaluated by two inter-laboratory "Round Robin" testing programs. In the final evaluation effort, participating laboratories were provided (single-blind) sand samples spiked with a #2 fuel oil, and a "real world" groundwater sample contaminated by a highly weathered fuel oil. Laboratory proficiency was evaluated using a Z-score approach. Data received from 23 laboratories performing the method without significant modifications are summarized below:

Matrix	# Labs Proficient	% Labs Proficient	Data from Proficient Laboratories		
			Fraction	%RSD	% Labs within +/- 40% mean value
soil	19	83	C_9-C_{18} Aliphatics	23	95
			C_{19}-C_{36} Aliphatics	30	89
			C_{11}-C_{22} Aromatics	19	100
			Total All Fractions (TPH)	17	100
water	20	87	C_9-C_{18} Aliphatics	84	22
			C_{19}-C_{36} Aliphatics	192	94
			C_{11}-C_{22} Aromatics	47	72
			Total All Fractions (TPH)	35	83

Laboratory and method performance on the water sample were adversely impacted by the relatively low concentrations of the aliphatic fractions (due to the low solubilities of these hydrocarbons in "real world" samples), and by breakthrough of naphthalenes into the aliphatic extract during fractionation. Improvements incorporated into this final method are expected to mitigate problems of this nature and significantly improve overall method performance.

1.12 This method is one way to quantify collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons within specified carbon number ranges. It has 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 incorporated into the method 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 diesel range 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_{18} aliphatic hydrocarbon range, and will therefore not be counted in the C_9 through C_{18} aliphatic hydrocarbon range;

(2) Depending upon the specific chromatographic column used, most branched C_{19} alkanes are expected to elute before n-nonadecane, the beginning marker compound for the C_{19} through C_{36} aliphatic hydrocarbon range, and will be conservatively counted in the more toxic C_9 through C_{18} aliphatic hydrocarbon range; and

(3) Depending upon the specific chromatographic column used, most cycloalkanes within the C_9 through C_{18} and C_{19} through C_{36} aliphatic hydrocarbon ranges will be counted within their proper range.

Based on the nature of petroleum releases encountered in the environment, the collective concentrations of the extractable aliphatic ranges as measured by the EPH 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).

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

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

- Such modifications or methodologies adequately quantify the petroleum hydrocarbon ranges, as defined in Sections 3.4 through 3.6 of this document, ensuring that any methodological uncertainties or biases are addressed in a manner that ensures protective (i.e., conservative) results and data (e.g., over, not under-quantification of the more toxic ranges);

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

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

1.14 Additional information and details on the MassDEP EPH approach are available at https://www.mass.gov/lists/policies-guidance-technical-support-for-site-cleanup .

1.15 This method should be used in conjunction with the current version of CAM IV B, "Quality Control Requirements and Performance Standards for the Analysis of Extractable Petroleum Hydrocarbons (EPH) in Support of Response Actions Under the Massachusetts Contingency Plan (MCP)". WSC-CAM-IV B was developed by MassDEP to complement this MassDEP EPH Method and to provide more detailed guidance regarding compliance with the QC requirements and performance standards of the MassDEP EPH Method.

2.0 SUMMARY OF METHOD AND DATA QUALITY OBJECTIVES

2.1 Samples submitted for EPH analysis are extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated in a Kuderna-Danish (K-D) apparatus. Sample cleanup and separation into aliphatic and aromatic fractions is accomplished using commercially available silica gel cartridges or prepared silica gel columns. The resulting two individual fraction extracts are re-concentrated to a final volume of 1 mL (i.e., an aliphatic extract and an aromatic extract). The concentrated extracts are then separately analyzed by a capillary column GC equipped with an FID. The resultant chromatogram from the analysis of the aliphatic extracts is used to determine the collective concentrations of aliphatic hydrocarbons within the C_9 through C_{18} and C_{19} through C_{36} ranges. The resultant chromatogram from the analysis of the aromatic extract is used to determine the collective concentration of aromatic hydrocarbons

within the C_{11} through C_{22} range, and is (optionally) used to determine the individual concentrations of Target PAH Analytes.

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.

2.3 This method is based on (1) USEPA Methods 8000D, 8100, 8270E, 3510C, 3520C, 3540C, 3541, 3545A, 3546, 3580A and 3630C, SW-846, "Test Methods for Evaluating Solid Waste"; (2) Draft *Method for Determination of Diesel Range Organics*, EPA UST Workgroup, November, 1990; and (3) *Modified DRO Method for Determining Diesel Range Organics*, Wisconsin Department of Natural Resources, PUBL-SW-141, 1992.

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

3.0 DEFINITIONS

3.1 **Aliphatic Hydrocarbon Standard** is defined as a 14 component mixture of the normal alkanes listed in Table 1. The compounds comprising the Aliphatic Hydrocarbon Standard are used to (a) define and establish retention time windows for the two aliphatic hydrocarbons ranges, and (b) determine average calibration or response factors that can in turn be used to calculate the collective concentration of aliphatic hydrocarbons in environmental samples within those hydrocarbon ranges.

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

3.3 **Aromatic Hydrocarbon Standard** is defined as a 17 component mixture of the PAHs listed in Table 2. The compounds comprising the Aromatic Hydrocarbon Standard are used to (a) define the individual retention times and determine the average calibration or response factors for each of the PAH analytes listed in Table 2, (b) define and establish the retention time window for the C_{11} through C_{22} Aromatic Hydrocarbon range, and (c) determine an average calibration or response factor that can in turn be used to calculate the collective concentration of aromatic hydrocarbons in environmental samples within the C_{11} through C_{22} hydrocarbon range.

3.4 **C_9 through C_{18} Aliphatic Hydrocarbons** are defined as all aliphatic petroleum hydrocarbon compounds which contain between nine and 18 carbon atoms. In the EPH method, C_9 through C_{18} aliphatic hydrocarbons are defined and quantitated as compounds which elute from n-nonane (C_9) to just before n-nonadecane (C_{19}).

3.5 **C_{19} through C_{36} Aliphatic Hydrocarbons** are defined as all aliphatic petroleum hydrocarbon compounds which contain between 19 and 36 carbon atoms. In the EPH method, C_{19} through C_{36} aliphatic hydrocarbons are defined and quantitated as compounds, which elute from n-nonadecane (C_{19}) to just after hexatriacontane (C_{36}).

3.6 **C_{11} through C_{22} Aromatic Hydrocarbons** are defined as all aromatic petroleum hydrocarbon compounds which contain between 11 and 22 carbon atoms. In the EPH method, C_{11} through C_{22} aromatic hydrocarbons are defined and quantitated as compounds which elute from naphthalene to just after benzo(g,h,i)perylene, excluding Target PAH Analytes.

3.7 **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.

3.8 **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

standard solution as initial calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.9 **Diesel PAH Analytes** are defined as naphthalene, 2-methylnaphthalene, phenanthrene, and acenaphthene, and are a subset of Target PAH Analytes. For most sites known to be contaminated by a release of diesel and/or #2 fuel oil only, Diesel PAH Analytes will be the only Target PAH Analytes of interest.

3.10 **Extractable Petroleum Hydrocarbons (EPH)** are defined as collective fractions of hydrocarbon compounds eluting from n-nonane to n-hexatriacontane, excluding Target PAH Analytes. EPH is comprised of C_9 through C_{18} Aliphatic Hydrocarbons, C_{19} through C_{36} Aliphatic Hydrocarbons, and C_{11} through C_{22} Aromatic Hydrocarbons.

3.11 **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.

3.12 **Fractionation Surrogate Standards** are compounds that are added to sample extracts immediately prior to fractionation at known concentrations to evaluate fractionation efficiency.

3.13 **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.

3.14 **Internal Standard (IS)** is a compound added to every calibration standard, blank, laboratory control sample (LCS), matrix spike, sample extract at a known concentration, prior to analysis. ISs are used as the basis for quantitation of the method's target analytes when GC/MS is utilized.

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

3.16 **Laboratory Control Sample Duplicate (LCSD)** is defined as a reagent water blank (when associated with aqueous samples) or clean sand 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.

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

3.18 **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.

3.19 **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 analyses 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.

3.20 **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.

3.21 **System Solvent Blank (SSB)** is defined as an aliquot of a method solvent (e.g., hexane or methylene chloride, pesticide-grade or better) that is directly injected into the GC system. The 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.

3.22 **Surrogate Standards** are compounds spiked into all samples, blanks, LCSs, and matrix spikes to monitor the efficacy of sample extraction, chromatographic, and calibration systems.

3.23 **Target PAH Analytes** are defined as the 17 PAH compounds listed in Table 2.

3.24 **Total Petroleum Hydrocarbons (TPH)** are defined as the collective concentration of all hydrocarbon compounds eluting from n-nonane to n-hexatriacontane, **excluding Target PAH Analytes**. TPH is equivalent to the summation of C_9 through C_{18} Aliphatic Hydrocarbons, C_{19} through C_{36} Aliphatic Hydrocarbons, and C_{11} through C_{22} Aromatic Hydrocarbons.

3.25 **Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds eluting from naphthalene through benzo(g,h,i)perylene.

3.26 **Unadjusted TPH** is defined as the collective concentration of all hydrocarbon compounds eluting from n-nonane to n-hexatriacontane, **including the Target PAH Analytes**.

3.27 All other terms are as defined in the most current version of SW-846, *Test Methods for Evaluating Solid Waste*, USEPA.

4.0 INTERFERENCES AND METHOD LIMITATIONS

4.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride.

4.2 High purity reagents must be used to minimize interference problems.

4.3 Cross-contamination can occur whenever a low-concentration sample is analyzed immediately after a high-concentration sample. To reduce carryover, the sample syringe must be rinsed between samples with solvent. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of an SSB 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.

4.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interference will vary considerably from one source to another depending upon the nature and complexity of the site being sampled. A silica gel SPE cleanup procedure is used to overcome many of these interferences, but some samples may require additional and more rigorous cleanup procedures which are beyond the scope of this method.

4.5 Other organic contaminants commingled with petroleum product releases, including chlorinated hydrocarbons, phenols, and phthalate esters, will be quantitated as TPH and EPH. If necessary and/or desirable, additional sample cleanup and/or analytical procedures may be employed to minimize or document the presence of such compounds.

4.6 The leaching of plasticizers and other compounds have been observed from commercially available silica gel cartridges used to fractionate EPH sample extracts. Concerns of this nature must be continuously monitored and documented by analysis of LMBs. Section 9.2 provides a procedure to eliminate or minimize this contamination.

4.7 Because of their weakly polar nature, naphthalene and substituted naphthalenes readily mobilize into the aliphatic extract if excessive amounts of hexane are used to elute the silica gel cartridge/column. Because these compounds constitute a significant percentage of the water-soluble fraction of fuel oils, this occurrence is especially problematic in the analysis of water samples. For this reason, the method requires the evaluation of the aliphatic fraction for the presence of naphthalene and 2-methylnaphthalene in the LCS/LCSD pair on a batch basis. The fractionation surrogate, 2-bromonaphthalene, is used to monitor sample-specific fractionation efficiency.

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 and 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 Gas Chromatograph System

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

6.1.2 Detector: An FID is required.

6.1.3 Chromatographic Column: The analytical column must adequately resolve the n-C_9 to n-C_{36} aliphatic hydrocarbon standard compounds and the Target PAH Analytes listed in Tables 1 and 2, respectively. The recommended analytical column is an RTX-5 capillary column (30-m x 0.32-mm internal diameter (I.D.), 0.25-µm film thickness [Restek Corp. or equivalent]).

6.1.4 Data Station: 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.

6.1.5 Autosampler: An autosampler capable of making 1 to 4 µL injections is recommended.

6.2 The following is a partial list of glassware used for this method:

6.2.1 1-L amber glass bottles.

6.2.2 4 oz. (120 mL) amber wide-mouth glass jars.

6.2.3 Vials:

- autosampler: 2-mL glass vials with Teflon-lined rubber crimp caps
- 10-mL vials with Teflon-lined caps

6.2.4 Glass funnels.

6.2.5 2-L Separatory funnels with Teflon stopcock (aqueous liquid-liquid extraction only).

6.2.6 K-D apparatus including 10-mL graduated concentrator tube, 500-mL Evaporative flask, & 3-ball Snyder column.

6.2.7 250-mL Erlenmeyer flasks.

6.2.8 25-mL graduated cylinder.

6.2.9 1-L graduated cylinder.

6.2.10 100-mL beakers.

6.2.11 Class "A" volumetric flasks: 10, 25, 50 and 100-mL.

6.2.12 Class "A" volumetric pipets: 1, 5 or 10-mL.

6.3 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.

6.4 An air or nitrogen blowdown apparatus, or equivalent sample concentration apparatus, is required to concentrate extracts.

6.5 Water bath: heated with a concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

6.6 Disposable pipets: Pasteur.

6.7 Microsyringes: 10-µL, 100-µL, 250-µL, 500-µL, 1000-µL.

6.8 Boiling chips.

6.9 Soxhlet, Soxtec or alternative extraction apparatus.

6.10 Drying oven.

6.11 Dessicator.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent Water: organic free water (American Society for Testing and Materials [ASTM] Type I reagent grade water).

7.1.2 Solvents: hexane, methylene chloride, and acetone; pesticide-grade or better. Store away from other solvents.

7.1.3 Sodium sulfate: (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

7.1.4 Ottawa and/or masonry sand: free of extractable petroleum hydrocarbons.

7.1.5 Silica Gel (5 - 10 grams), either prepared and packed by the laboratory, or purchased in 5 g/15-mL cartridges from a commercial vendor. Silica gel prepared and packed by the laboratory should be activated at 130ºC for at least 16 hours, and heated to 150-160ºC for several hours before use. Refer to Section 9.2.2 for guidance on the use of silica gel.

NOTE: Leaching of plasticizers and other compounds have been observed from commercially prepared silica gel cartridges, and must be monitored and documented by analyses of LMBs. Refer to Section 9.2 for a procedure to eliminate or minimize this contamination.

NOTE: **Silica gel is hygroscopic**. Unused cartridges readily absorb moisture from ambient air if not properly sealed. To preclude moisture adsorption, which adversely effects cartridge performance, unused cartridges must be stored in a properly-maintained desiccator prior to use.

7.2 Stock Standard Solutions

Prepare stock standard solutions at approximately 1000 ng/µL, or purchase as certified solutions.

7.2.1 Aromatic Hydrocarbon Standard: The Aromatic Hydrocarbon Standard consists of the 17 PAH compounds listed in Table 2, a surrogate compound (i.e., ortho-terphenyl [OTP]) and fractionation surrogate compounds. Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in methylene chloride and dilute to volume in a 10-mL volumetric flask.

7.2.2 Aliphatic Hydrocarbon Standard: The Aliphatic Hydrocarbon Standard consists of the 14 normal alkanes listed in Table 1, naphthalene, 2-methylnaphthalene, and a surrogate compound (i.e., 1-chloro-octadecane [COD]). Prepare stock standard solutions by accurately weighing approximately 0.0100 g of pure material. Dissolve the material in hexane and dilute to volume in a 10-mL volumetric flask.

7.2.3 Transfer each stock standard into a PTFE-lined screw cap vial. Store the vials (protected from light) at ≤6 °C or as recommended by the standard manufacturer. Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.2.4 Calibration standards are prepared by serial dilution of the stock standard as described in Section 7.3.

7.3 EPH Calibration Standards: Prepare Aromatic and Aliphatic Hydrocarbon calibration standards from the stock standard solutions. At a minimum, five different concentrations are required for a valid calibration curve by adding volumes of the stock standard solutions to volumetric flasks and diluting to volume with methylene chloride and hexane, respectively. The surrogate OTP and the fractionation surrogates are included in the Aromatic Hydrocarbon calibration standard; the surrogate COD, naphthalene, and 2-methylnaphthalene are included in the Aliphatic Hydrocarbon calibration standard. The calibration concentrations must be evenly dispersed over the full working range of the detector with the lowest calibration point corresponding to the RL for Target PAH Analytes. The highest concentration defines the maximum upper working range of the calibration curve. Table 3 provides recommended concentrations for each calibration standard for a 5-point initial calibration of hydrocarbon ranges and Target PAH Analytes

7.4 Petroleum Reference Spiking Solution: The Petroleum Reference Spiking Solution consists of an API or commercial diesel fuel standard. Prepare stock standard solutions by accurately weighing approximately 0.02500 g of neat product. Dissolve neat product in acetone and dilute to volume in a 10-mL volumetric flask. An appropriately diluted aliquot of the stock solution may be used to evaluate method performance

7.5 Surrogate Standards

7.5.1 Surrogate standards are used to monitor the efficiency of sample extraction, chromatographic, and calibration systems.

7.5.2 The recommended surrogate standards are COD and OTP. Alternatively, 5-alpha-androstane may also be used as an aliphatic fraction surrogate without qualification.

7.5.3 The surrogate standard COD is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in hexane.

7.5.4 The surrogate standard OTP is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in methylene chloride.

7.5.5 Surrogate Spiking Solution: The recommended surrogate spiking solution is comprised of a mixture of the COD and OTP surrogate standards. Prepare a surrogate spiking solution which contains the surrogate standards at a concentration of 40 ng/µL in acetone or methanol. Each sample, LMB, LCS, and matrix spike is fortified with a specified volume of the surrogate spiking solution in order to yield a final concentration of 40 ug/mL (on column, prior to correction for

preparation factors). The use of higher concentrations is permissible and advisable when spiking highly contaminated samples.

7.6 Fractionation Surrogate Standards

7.6.1 The fractionation surrogate standards are added to the sample (hexane) extract just prior to fractionation. The purpose of the fractionation surrogate standards is to monitor the efficiency of the fractionation process, and ensure that unacceptable quantities of naphthalene and substituted naphthalenes are not being eluted into the aliphatic extract.

7.6.2 The recommended fractionation surrogate standard is 2-Bromonaphthalene. Other alternative fractionation surrogate compounds, including 2-Fluorobiphenyl are permissible, provided that a demonstration is made that such compounds exhibit polarities/fractionation properties similar to naphthalene.

7.6.3 The fractionation surrogate standards are prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in methylene chloride.

7.6.4 Fractionation Surrogate Spiking Solution: is comprised of 2-Bromonaphthalene and 2-Fluorobiphenyl (optional) prepared in hexane at concentrations of 40 ng/µL. An aliquot of 1 mL of the fractionation surrogate spiking solution is added to the 1 mL EPH sample extract prepared in accordance with the provisions of Sections 9.1.1 and 9.1.2. Alternative concentrations/volumes of the fractionation surrogate spiking solution are permissible.

7.7 Internal Standards (ISs)

7.7.1 ISs are compounds with similar physical and chemical properties, and chromatographic compatibility with an analytical method's target analytes. ISs are added to all samples, both for analysis and quality control, at a known concentration and carried through the entire analytical process. ISs are used as the basis for quantification of Target PAH Analytes (and hydrocarbon ranges) for the applied analytical method. For the EPH method, ISs are only utilized when GC/MS is utilized for quantification.

7.7.2 The recommended IS for the EPH Method is 5-alpha-androstane when a modified SW-846 8270E is used to quantify the Target PAH Analytes and the fractionated aliphatic and/or aromatic hydrocarbon range concentrations using GC/MS.

7.7.3 The IS is prepared by accurately weighing approximately 0.0500 grams of pure material in a 10-mL volumetric flask. Dissolve the material in methylene chloride or hexane.

7.7.4 An aliquot of 10 µL of the IS stock standard is added to each 1 mL EPH sample extract prepared in accordance with Section 9.3. Alternative concentrations/volumes of the IS spiking solution are permissible.

7.8 Matrix Spiking Solution

7.8.1 The matrix spiking solution, consisting of all normal alkanes in Table 1 and all PAHs in Table 2, is prepared in methanol or acetone at concentrations between 50 - 150 ng/µL (The concentration should be between the mid and upper level of calibration).

7.8.2 The samples selected as the matrix spike are fortified with a specified volume of the matrix spiking solution in order to yield a final concentration of 50-150 ug/mL (on column, prior to correction for preparation factors).

Analytical Note: The matrix spiking solution should always be brought to room temperature before use to promote dissolution of the highest boiling (marginal solubility) hydrocarbon standards.

7.9 Fractionation Check Solution

7.9.1 The Fractionation Check Solution is used to monitor the fractionation efficiency of the silica gel cartridge/column, and establish the optimum hexane volume required to efficiently elute aliphatic hydrocarbons while not allowing significant aromatic hydrocarbon breakthrough.

7.9.2 Prepare a Fractionation Check Solution in hexane containing 200 ng/µL of the Aliphatic Hydrocarbon standard (C_9-C_{36} alkanes) and 200 ng/µL of the Aromatic Hydrocarbon standard (Target PAH Analytes). The final solution will contain 14 alkanes and 17 PAHs at concentrations of 200 ng/µL each. Alternative concentrations are permissible.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Aqueous Samples

8.1.1 It is good practice to instruct field personnel to collect aqueous samples in duplicate. Samples must be collected in 1-liter amber glass bottles with Teflon-lined screw caps.

8.1.2 Aqueous samples must be preserved at the time of sampling by the addition of a suitable acid to reduce the pH of the sample to less than 2.0. This may be accomplished by the addition of 5 mL of 1:1 hydrochloric acid (HCl) to a 1 liter sample. The uses of alternative acids are permissible. Following collection and addition of acid, the sample must be cooled to 0-6° C.

8.1.3 A chain-of-custody form must accompany all sample bottles and must document the date and time of sample collection and preservation method used. The laboratory must determine the pH of all water samples as soon as possible after sample receipt and prior to sample extraction. Any sample found to contain a pH above 2 must be so noted on the laboratory/data report sheet and the pH must be adjusted as soon as possible.

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

8.1.5 Aqueous samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

8.2 Soil/Sediment Samples

8.2.1 Soil and sediment samples are collected in 4-oz. (120-mL) amber wide-mouth glass jars with Teflon-lined screw caps.

8.2.2 Soil and sediment samples must be cooled to 0-6° C immediately after collection.

8.2.3 A chain-of-custody form must accompany all sample bottles and must document the date and time of sample collection and preservation method used.

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

8.2.5 Soil and sediment samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

8.2.6 Alternatively, samples may be frozen (- 10°C) in the field or in the laboratory. Samples frozen in the laboratory must be preserved at 0-6° C from the time of sampling and frozen within 24 hours of the time of collection.

8.3 A summary of sample collection containers, preservation, and holding times is provided in Table 4.

9.0 EXTRACTION AND ANALYTICAL PROCEDURES

9.1 Overview of Sample Extraction Procedures

Samples are extracted using methylene chloride and solvent-exchanged into hexane. EPH extraction may be accomplished manually or by automated methods. In this section a detailed description of manual separatory funnel liquid-liquid extraction for aqueous samples (SW-846 Method 3510) and the Soxhlet extraction procedure (SW-846 Method 3540) for soils and/or sediments are presented to demonstrate general extraction concepts for petroleum products. The applicable SW-846 Method should be consulted for specific details for the other approved EPH extraction procedures.

NOTE: For optimum performance, the sample volumes/weights, solvent volumes, and final extract volumes cited in Sections 9.1.1 and 9.1.2 are recommended. Alternate volumes can be used as long as comparable RLs are achieved.

The complete list of approved EPH extraction procedures for aqueous and soil/sediment samples is presented in Table 5. Alternative extraction procedures other than those listed are acceptable, provided that the laboratory can document acceptable matrix- and petroleum product-specific performance. However, use of an alternative extraction procedure is considered a "significant modification" of the EPH method pursuant to Section 11.3.1.1 and as such would preclude obtaining "Presumptive Certainty" status for any analytical data produced using an alternative EPH extraction procedure

9.1.1 Aqueous Extraction by Separatory Funnel Liquid-Liquid Extraction

9.1.1.1 Mark the meniscus on the 1-liter sample bottle (for later volume determination) and transfer the contents to a 2-liter separatory funnel. For LMBs, LCSs, and LCSDs, pour 1 liter of reagent water into the separatory funnel. For all samples, LMBs, LCSs, LCSDs and matrix spikes add the specified volume of the surrogate spiking solution (see Section 7.5) directly to the separatory funnel. For samples selected for matrix spikes, also add the specified volume of the matrix spiking solution (see Section 7.8).

9.1.1.2 Check the pH of the sample with wide-range pH paper. Note the pH in the laboratory notebook. The pH of the sample must be adjusted to pH <2.

9.1.1.3 Add 60 mL methylene chloride to the sample bottle to rinse the inner walls of the container, then add this solvent to the separatory funnel.

9.1.1.4 Seal and shake the separatory funnel vigorously for at least three (3) minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once.

9.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask.

9.1.1.6 Repeat the extraction two more times using additional 60 mL portions of solvent. Combine the three solvent extracts in a 250-mL Erlenmeyer flask. (Steps 9.1.1.3 to 9.1.1.5)

9.1.1.7 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked and transfer this water to a graduated cylinder.

9.1.1.8 Assemble a K-D concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.1.9 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate or other suitable drying agent. Collect the dried extract in the K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 to 30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

9.1.1.10 Add one or two clean boiling chips to the K-D flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.1.11 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column. Concentrate the extract to less than 10 mL, as described in Section 9.1.1.10, raising the temperature of the water bath, if necessary, to maintain proper distillation.

9.1.1.12 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto an air blowdown apparatus. Adjust the extract volume to 1 mL under a gentle stream of nitrogen or air. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher. If a TPH analysis is to be conducted, without fractionation, proceed to Section 9.3.3.

Analytical Note: Due caution must be exercised during blowdown to avoid losses of the more volatile (C_9 through C_{12}) EPH components. The fractionation extract (or any extract) volume should never be reduced below 1 mL in this or any other step to minimize volatilization losses.

9.1.1.13 Add 1 mL of the concentrated fractionation surrogate spiking solution (see Section 7.6) to the 1 mL hexane extract. Alternatively, add 20-50 ng each of the fractionation surrogate standards using a microliter syringe (up to 10 uL volume).

Analytical Note: If the latter alternative is exercised, only a single extract will be available for fractionation unless the spiked extract is further diluted. Such dilution may not be advisable for samples with Target PAH Analytes or hydrocarbon ranges at or near the method's RL.

9.1.1.14 Record the sample preparation information for the extraction and concentration steps. At a minimum, record the date, sample laboratory number, sample volume, volume and concentration of added surrogates and matrix spike solutions, the original pH, final extract volume, and any deviations or problems associated with the extraction of the samples.

9.1.1.15 The 2 mL extract (1 mL extract + 1 mL fractionation surrogate) is now ready to be cleaned and fractionated using silica gel SPE cartridges. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.1.16 For cleanup and fractionation, refer to Section 9.2.

9.1.2 Soil and/or Sediment Extraction using Soxhlet Extraction

9.1.2.1 Blend 10 g of the solid sample with 10 g anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. Add the specified volume of the surrogate spiking solution (see Section

7.5) to all samples, LMBs, LCSs, LCSDs and matrix spikes. Thoroughly mix the surrogate spiking solution into the sample. For samples selected for matrix spikes, also add the specified volume of the matrix spiking solution (see Section 7.8). Thoroughly mix the matrix spiking solution(s) into the sample.

9.1.2.2 Place 300 mL of methylene chloride into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours. The volume of methylene chloride should be adjusted to accommodate the size of the round-bottom flask utilized.

9.1.2.3 Allow the extract to cool after the extraction is completed.

9.1.2.4 Assemble a K-D concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

9.1.2.5 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate or other suitable drying agent. Collect the dried extract in the K-D concentrator. Rinse the extractor flask with 100 to 125 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

9.1.2.6 Add one or two clean boiling chips to the K-D flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the top of the Snyder column. Concentrate the extract to less than 10 mL, as described in Section 9.1.2.6, raising the temperature of the water bath, if necessary, to maintain proper distillation.

9.1.2.8 Remove the Snyder column and evaporation flask from the 10-mL concentrator tube. Place the concentrator tube containing the hexane extract onto an air blowdown apparatus. Adjust the extract volume to 1 mL under a gentle stream of nitrogen or air. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher. If a TPH analysis is to be conducted without fractionation, proceed to Section 9.3.3.

Analytical Note: Due caution must be exercised during blowdown to avoid losses of the more volatile (C_9 through C_{12}) EPH components. The fractionation extract (or any extract) volume should never be reduced below 1 mL in this or any other step to minimize volatilization losses.

9.1.2.9 Add 1 mL of the concentrated fractionation surrogate spiking solution (see Section 7.6) to the 1 mL hexane extract. Alternatively, add 20-50 ng each of the fractionation surrogate standards using a microliter syringe (up to 10 uL volume).

Analytical Note: If the latter alternative is exercised, only a single extract will be available for fractionation unless the spiked extract is further diluted. Such dilution may not be advisable for samples with Target PAH Analytes or hydrocarbon ranges at or near the method's RL.

9.1.2.10 Record the sample preparation information for the extraction and concentration steps. At a minimum, record the date, sample laboratory number, sample weight, volume and concentration of added surrogates and matrix spike solutions, extraction start and stop times,

final extract volume and any deviations or problems associated with the extraction of the samples.

9.1.2.11 The 2 mL extract (1 mL extract + 1 mL fractionation surrogate) is now ready to be cleaned and fractionated using silica gel SPE cartridges. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.2.12 For cleanup and fractionation, refer to Section 9.2.

9.2 Silica Gel Cleanup and Fractionation

NOTE: The Silica Gel Cleanup and Fractionation step is a critical and highly sensitive procedure. Small changes in the volumes of eluting solvents, fractionation equipment, and/or fractionation techniques can significantly impact the proportion of hydrocarbons segregated in either the aliphatic or aromatic fractions. Considerable care and attention is required to ensure satisfactory results.

9.2.1 Each sample fractionation requires 1 mL of sample extract. Because 2 mL of sample extract are available, two fractionations may be undertaken for each sample. Refractionation would be necessary if problems are experienced during the initial fractionation effort, if unacceptable breakthrough is noted for naphthalene and 2-methylnaphthalene in the LCS and/or LCSD, and/or if unacceptable recoveries are noted for the fractionation surrogate standard(s). The extra volume of sample extract is also provided to facilitate initial (unfractionated) TPH screening of a sample, to obtain a GC/FID "fingerprint", and/or to determine whether sufficient total hydrocarbons are present to warrant fractionation and comparison to risk-based cleanup standards.

9.2.2 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is used for separating analytes from interfering compounds of a different chemical polarity. Silica gel is also used to separate petroleum distillates into aliphatic and aromatic fractions.

A 5 g/15-mL SPE silica gel cartridge is commercially available. Alternatively, the use of self-packed columns of activated silica gel may also be used. The use of activated silica gel for general column chromatographic applications is described in detail in SW-846 Method 3630C.

To ensure satisfactory fractionation, silica gel/cartridges must not be overloaded. It is recommended that loading be limited to no more than 5 mg total hydrocarbons/gram silica gel; for a 1 mL extract fractionated on a 5 gram silica gel cartridge, this would equate to a hydrocarbon extract loading of no greater than 25,000 µg/mL. It should be noted that overloading the column may result in a premature breakthrough of the C_{11}-C_{22} aromatic hydrocarbon range. If overloading is encountered, the sample must be re-fractionated at a dilution appropriate for the column's maximum loading capacity.

Unsealed silica gel/cartridges must be stored in a properly-maintained desiccator to avoid inadvertent adsorption of ambient moisture. Silica gel that has been exposed to moisture may perform erratically resulting in poor performance manifested by naphthalene/2-methylnaphthalene and fractionation surrogate breakthrough.

Analytical Note:	**Air-drying of the cartridges may adversely affect silica gel performance and is not advised.**

9.2.3 If concerns exist over the presence of contaminants in the silica gel/cartridge, pre-rinse the column with 30 mL of methylene chloride.

9.2.3.1 Rinse the column with 30 mL of hexane, or 60 mL if pre-rinsed with methylene chloride per Section 9.2.3. Let the hexane flow through the column until the head of the liquid in the column is just above the column frit. Close the stopcock to stop solvent flow. Discard the collected hexane.

9.2.3.2 Load 1.0 mL of the combined sample extract and fractionation surrogate solution onto the column. Open the stopcock, and start collecting elutant immediately in a 25-mL volumetric flask labeled "aliphatics".

9.2.3.3 Just prior to exposure of the column frit to the air, elute the column with an additional 19 mL of hexane, so that a total of approximately 20 mL of hexane is passed through the column.

It is essential that "plug flow" of the sample extract be achieved through the silica gel cartridge/column. Hexane should be added in 1-2 mL increments or dropwise using a pipet, with additions occurring when the level of solvent drops to the point just prior to exposing the column frit to air. The use of a stopcock is mandatory. Care must be taken to ensure that the silica gel is uniformly packed in the column. The analyst must be cognizant of any channeling, streaking, or changes in the silica gel matrix during fractionation; if any of these occur, the procedure must be repeated with another 1 mL volume of sample extract.

The amount of hexane used during fractionation is critical. Excessive hexane - as little as 0.5 mL - can cause significant elution of lighter aromatics into the aliphatic fraction. Insufficient hexane will cause low recoveries of the aliphatic fraction. The volume of the hexane fractionation elutriate should not exceed 20 mL.

9.2.3.4 The Fractionation Check Solution described in Section 7.9 must be used to evaluate each new lot of silica gel /cartridges to re-establish the optimum volume of hexane elutriate. See Appendix 5, Section 5.0 for optimization specifications.

It is not uncommon to encounter inconsistent cartridge weights, mesh sizes and/or variable fractionation performance within the same lot of silica gel cartridges. It may be advisable to perform additional intra-lot fractionation performance checks particularly for larger lot sizes (500) of silica gel cartridges.

9.2.3.5 Following recovery of the aliphatic fraction, elute the column with 20 mL of methylene chloride and collect the eluant in a 25 mL volumetric flask. Label this fraction "aromatics".

9.3 Final Sample Extract Concentration

9.3.1 Transfer the contents of the 25.0 mL "aliphatics" (in hexane) and "aromatics" (in methylene chloride) volumetric flasks into separate labeled graduated concentrator tubes. Concentrate each of the extracts to a final volume of 1 mL under a gentle stream of air or nitrogen.

Analytical Note: Due caution must be exercised during blowdown to avoid losses of the more volatile (C_9 through C_{12}) EPH components. The fractionation extract (or any extract) volume should never be reduced below 1 mL in this or any other step to minimize volatilization losses.

9.3.2 Transfer the final 1 mL extracts from each concentrator tube to labeled 2-mL glass autosampler vials with Teflon-lined rubber crimp caps. If appropriate, add an IS at the appropriate concentration.

9.3.3 Proceed with the analysis in accordance with Section 9.8. Analyze all QC samples under the same conditions as that used for samples.

9.4 Determination of Percent Moisture

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

9.4.2 Transfer 5 to 10 g of sample into a tared (± 0.1 g) crucible and determine "wet weight". Dry this 5 to 10 g sample overnight at 105°C. Allow the crucible to cool in a desiccator and reweigh (± 0.1 g). Re-desiccate and verify "dry weight". Calculate the percent moisture of the sample using the equation provided in Section 9.9.3 (Equation 10). Refer to ASTM Method D2216, *Determination of Moisture Content of Soils and Sediments*, for more detailed analytical and equipment specifications.

9.5 Analytical Conditions

9.5.1 Recommended analytical conditions are presented below. A chromatographic column with equivalent chromatographic properties, as described in Section 6.1.3, or alternative chromatographic conditions may be substituted to improve resolution of extractable petroleum hydrocarbons.

Chromatographic Column:	30 m x 0.32 mm I.D., 0.25 µm film thickness Restek RTX-5
Oven Temperature Program	Initial oven temperature 60°C, hold time 1 min; to 290 °C @ 8°C/min, hold time 6.75 min
Total Run Time:	36.5 min
Sample/autosampler Injection	1-4 uL
Gas Flow Rates:	Carrier gas – Helium @ 2 to 3 mL/ min Oxidizer – Air @ 400 mL/min Fuel – Hydrogen @ 35 mL/min Make up – Air @ 30.0 mL/min
Injection Port Temperature:	285°C
Column Inlet Pressure:	15 p.s.i.g.
Detector Temperature:	315°C (FID)
Linear Velocity	50 cm/sec

9.5.2 GC Maintenance

9.5.2.1 Capillary columns: Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert.

9.5.2.2 Break off the first few inches, up to one foot, of the injection port side of the column.

9.5.2.3 Remove the column and solvent backflush according to the manufacturer's instructions.

9.5.2.4 Bake out the column at the maximum temperature of the temperature program. If these procedures fail to eliminate a column degradation problem, it may be necessary to replace the column.

9.6 Retention Time Windows

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

9.6.2 Calculate the standard deviation of the three absolute Rts for each individual compound in the Aromatic Hydrocarbon Standard, the Aliphatic Hydrocarbon Standard, and all surrogates and internal standards.

9.6.3 The Rt window is defined as plus or minus three times the standard deviation of the absolute Rt for each compound in the Aliphatic and Aromatic Hydrocarbon Standards. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.6.4 In those cases where the standard deviation for a particular standard is close to zero, the default value of 0.1 minutes should be used. Alternatively, the laboratory may substitute the standard

deviation of a closely eluting structurally similar compound to develop a representative statistically-derived Rt window.

9.6.5 The laboratory must calculate Rt windows for each compound in the Aliphatic and Aromatic Hydrocarbon Standards on each GC column and whenever a new GC column is installed. These data must be retained by the laboratory.

9.6.6 EPH Rt windows are defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ending 0.1 minutes after the Rt of the ending marker compound, except for n-C_{19}, which is both a beginning and ending marker compound for two different ranges.

The C_9 - C_{18} Aliphatic Hydrocarbon range ends immediately (0.1 min) before the elution of the n-C_{19} peak. The C_{19} - C_{36} Aliphatic Hydrocarbon range begins 0.1 min before the elution of the n-C_{19} peak; therefore there is no overlap of the two ranges and the n-C_{19} peak is only included in the C_{19} - C_{36} Aliphatic Hydrocarbon range.

EPH marker compounds and windows are summarized in Table 6.

9.6.7 If a TPH analysis is done without fractionation, TPH Rt windows are defined as beginning 0.1 minutes before the Rt of n-Nonane and ending 0.1 minutes after the Rt of n-Hexatriacontane.

9.7 Calibration

9.7.1 The EPH calibration standards are used to calibrate the GC/FID system. Two distinct calibration operations are necessary.

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

9.7.1.2 Collective Aliphatic/Aromatic Hydrocarbon Ranges: CFs are calculated for C_9-C_{19} aliphatic hydrocarbons and C_{19}-C_{36} aliphatic hydrocarbons based upon a correlation between the TOTAL concentration of aliphatic EPH Components eluting within the range of interest and the total FID area count of the applicable EPH component peaks. A CF is calculated for C_{11}-C_{22} aromatic hydrocarbons based upon a correlation between the concentration of the Target PAH Analytes used to calibrate this range and the total FID area count of the Target PAH Analytes. Specified EPH Components are designated marker compounds to define the beginning and end of the hydrocarbon ranges (see Table 6). A listing of the hydrocarbon range compounds used to establish CFs for each hydrocarbon range of interest and their individual component concentration (µg/L) is provided in Tables 1 through 3.

9.7.2 Initial Calibration

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

9.7.2.2 An internal standard calibration procedure is not recommended for this method except when GC/MS is used to quantify Target PAH Analytes and hydrocarbon ranges (see Section 9.10).

9.7.2.3 The use of CFs is the preferred approach to determine the relationship between the detector response and the Target PAH Analyte and hydrocarbon range concentrations. It is also permissible to utilize linear regression (see Sections 9.7.2.13 and 9.7.2.14). The linear regression approach for Target PAH Analytes and hydrocarbon ranges is described in Appendix 4. The use of non-linear regression is not allowed in this method and is considered a significant modification as discussed in Section 11.3.1.1.

9.7.2.4 An initial calibration is performed using a minimum of five different concentrations of EPH calibration standards as per Section 7.3. Recommended Target PAH Analyte and hydrocarbon range calibration standard concentrations are provided in Table 3. 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 PAH Analytes (see Section 12.0).

9.7.2.5 Introduce each calibration standard into the gas chromatograph using the injection volume (e.g., 1 to 4 µL) that will be used to introduce the "actual" samples and according to the procedures specified in Section 9.8.

9.7.2.6 Target PAH Analytes and Surrogates - Tabulate the FID area response against the concentration for each Target PAH Analyte and surrogate, and calculate a CF for each compound using Equation 1. Perform this calculation for each Target PAH Analyte and surrogate.

Equation 1: Calibration Factor for Target PAH Analytes and Surrogates

$$Calibration\ Factor\ (CF) = \frac{area\ \ of\ \ peak}{concentration\ injected\ (ng/uL)}$$

9.7.2.7 Hydrocarbon Ranges - Establish retention time windows for the hydrocarbon ranges using the EPH component marker compounds shown in Table 6.

9.7.2.8 Calculate a CF for the C_9-C_{18} aliphatic hydrocarbon range using the following steps.

Sum the individual FID peak areas of the six EPH Components that are used to establish an average range CF for C_9-C_{18} aliphatic hydrocarbons. It is important to note that these integrations must be performed using a valley-to-valley approach for each of the individual peaks that comprise this range. The sum of each of these areas is used in the subsequent calculation. Note: Do not include the areas of any surrogate standard or naphthalene and 2-methylnaphthalene in calculating a hydrocarbon range CF.

Using this total area, calculate the C_9-C_{18} aliphatic hydrocarbon range CF using Equation 2.

Equation 2: Calibration Factor for Hydrocarbon Range

$$Range\ CF = \frac{Area\ summation\ of\ range\ components}{Total\ concentration\ injected\ (ng\ /uL)}$$

9.7.2.9 Calculate a CF for the C_{19}-C_{36} aliphatic hydrocarbon range using the following steps.

Sum the individual FID peak areas of the eight EPH Components that are used to establish an average range CF for C_{19}-C_{36} aliphatic hydrocarbons. It is important to note that these integrations must be performed using a valley-to-valley approach for each of the individual peaks that comprise this range. The sum of each of these areas is used in the subsequent calculation. Note: Do not include the area of any surrogate standard in calculating a hydrocarbon range CF.

Using this total area, calculate the C_{19}-C_{36} hydrocarbon range CF using Equation 2.

9.7.2.10 Calculate a CF for the C_{11}-C_{22} aromatic hydrocarbon range using the following steps.

Use the individual FID peak areas of the 17 Target PAH Analytes which are used to establish an average range CF for C_{11}-C_{22} aromatic hydrocarbons. It is important to note that integration must be performed using a valley-to-valley approach for each of the

individual peaks that comprise this range. The sum of each of these areas is used in the subsequent calculation. Note: Do not include the area of any surrogate standard in calculating a hydrocarbon range CF.

Using this area, calculate the C_{11}-C_{22} aromatic range CF using Equation 2.

9.7.2.11 Calculate the average CF for each of the Target PAH Analytes, the surrogates, and each hydrocarbon range.

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

Equation 3: Percent Relative Standard Deviation

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

where:

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

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

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

NOTE: Use of non-linear calibration is not allowed and is considered a Significant Modification as per Section 11.3.1.1.

9.7.2.14 In order for the linear regression model to be used for quantitative purposes, the correlation coefficient (r) must be ≥0.99. In addition, the resulting calibration curve from the linear regression must be verified by recalculating concentrations of the Target PAH 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.

9.7.2.15 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.

9.7.2.16 The initial calibration must be verified through the analysis of an 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 standards and must be analyzed immediately following the initial calibration. The ICV should be prepared at a mid-range calibration curve concentration.

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

Equation 4: Percent Recovery

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

where:

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

9.7.3 Continuing Calibration

9.7.3.1 A Continuing Calibration Standard must be analyzed daily prior to sample analysis, after every 20 samples or every 24 hours (whichever is more frequent), and at the end of the analytical sequence. It should be noted that the Percent Differences (%Ds) are calculated (Equation 5) when CFs are used for the initial calibration and Percent Drifts (Equation 4-5, Appendix 4) are calculated when calibration curves using linear regression are used for the initial calibration.

9.7.3.2 The concentration of the EPH Continuing Calibration Standard must be near the midpoint of the calibration curve.

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

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

Equation 5: Percent Difference

$$\%D = [(CFc) - (CFI)]/[(CFI)]$$

where:

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

9.7.3.5 The %D or Percent Drift for each Target PAH Analyte, surrogate, and hydrocarbon range must be $\leq$25. If more than one Target PAH Analyte or hydrocarbon range fails to meet the applicable criterion, the instrument must be recalibrated. Otherwise, sample analysis may proceed. For the closing continuing calibration standard (analyzed after every 20 samples, every 24 hours, or at end of analytical sequence), four compounds may exhibit %Ds or Percent Drifts greater than 25% but less than 40%.

9.7.4 For TPH analysis without fractionation, CFs are developed based upon the response of all 14 aliphatic components using Equation 2.

9.7.5 Daily Rt Windows: The range Rt windows must be established daily based upon the Rt of the marker compounds in the EPH Continuing Calibration Standard. Use the absolute Rt for each analyte in the Continuing Calibration Standard as the midpoint of the window for that day. The daily Rt window equals the midpoint $\pm$ 3 times the standard deviation determined in Section 9.6. Alternatively, the default value of 0.1 minutes may be used for the daily Rt window. The marker compounds used for each hydrocarbon range are defined in Table 6.

9.8 GC Analysis

9.8.1 Samples are analyzed in a group referred to as an analytical batch. For methods that require extraction prior to analysis, such as EPH, the number of samples that comprise an analytical batch is generally limited to 20 samples plus the requisite QC samples processed concurrently with the extraction batch. The analytical sequence begins with instrument calibration (initial or continuing) followed by up to 20 samples interspersed with blanks and other QC samples and closed with a mid-range Continuing Calibration Standard. The analytical sequence ends when one or more analytical batches have been processed or when any required qualitative and/or quantitative QC criteria are exceeded, whichever comes first.

9.8.2 Aliphatic and aromatic extracts are introduced into the gas chromatograph by direct injection.

9.8.3 Inject 1 to 4 µL of the sample extract using the solvent flush technique. Smaller volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL and the resulting peak size in area units. It is required that the sample and calibration standard injection volume be consistent.

9.8.4 Identification of Target PAH Analytes

- Tentative identification of a Target PAH Analyte occurs when a peak from a sample chromatogram falls within the daily Rt window. Confirmation on a second GC column or by GC/MS analysis may be necessary, if warranted by the project's data quality objectives.
- Validation of GC system qualitative performance must be accomplished by the analysis of mid-level standards within the analysis sequence. If the Rts of the Target PAH Analytes fall outside their daily Rt window in the standards, the system is out of control. In such cases, the cause of the non-conformance must be identified and corrected.

9.8.5 Aliphatic and aromatic hydrocarbon ranges of interest in samples 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.

9.8.6 **In samples, collective peak area integration for the hydrocarbon ranges, or TPH, must be <u>from baseline</u> (i.e., must include the unresolved complex mixture "hump" areas).** For the integration of individual Target PAH 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 PAH Analytes, surrogate compounds, and internal standards.

9.8.7 Baseline correction using a SSB is **only** permissible for the calculation of aliphatic and aromatic hydrocarbon range concentrations when conducted in accordance with the procedures and requirements specified in Section 11.2.5.

9.8.8 If the Target or Diesel PAH Analytes are to be quantitated using this method, and the response for an individual Target PAH analyte exceeds the linear range of the system, dilute the extract and reanalyze. The samples/extracts must be diluted so that all peaks fall within the linear range of the detector.

9.8.9 For non-target analytes eluting in the aliphatic, aromatic or TPH 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 component within the hydrocarbon range that is shown to be within the linear range of the detector.

9.8.10 Under circumstances that sample dilution is required because the concentration of one or more of the Target PAH Analytes exceeds the concentration of their respective highest calibration standard,

any non-target peak eluting within any aliphatic or aromatic hydrocarbon range exceeds the peak height documented for the highest range-specific calibration standard, or anytime a saturated chromatographic peak (flat-topped peak) is encountered, the RL for each Target PAH Analyte and/or hydrocarbon range must be adjusted (increased) in direct proportion to the Dilution Factor (D).

Where:

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

And the revised RL for the diluted sample, RL_d:

RL_d = D * Lowest Calibration Standard for Target PAH Analyte

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

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

9.9 Calculations

The concentrations of Target PAH Analytes and hydrocarbon ranges in a sample may be determined from the peak area response, using the CFs determined in Section 9.7.2. If linear regression was used for calibration, refer to Appendix 4 for sample concentration calculations.

9.9.1 Individual Target PAH Analytes and Surrogate: The average CF from the initial calibration is used to calculate the concentration of an analyte or surrogate detected in the sample. Equations 6 and 7 are used to calculate the concentrations of Target PAH Analytes and the surrogate in aqueous and non-aqueous samples, respectively.

Equation 6: Aqueous Samples (Target PAH Analytes and Surrogates)

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

where:

Ax = Area count for the Target PAH Analyte or surrogate
D = Dilution factor (see Section 9.8.10)
CF = Average CF for Target PAH Analyte or surrogate
V_t = Volume of total extract, µL (including fractionation surrogate volume)
V_s = Volume of sample extracted, mL.

Equation 7: Non-Aqueous Samples (Target PAH Analytes and Surrogates)

$$Conc\ Analyte\ (ug/kg) = \frac{(A_x)(V_t)(D)}{(W_d)(CF)}$$

where:

W_d = Dry weight of sample, g (see Equations 10 through 12)
A_x, V_t, D, and CF have the same definition as described above for Equation 6.

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

9.9.2 Hydrocarbon Ranges

When calculating the aliphatic and aromatic hydrocarbon range concentrations, the laboratory **must** include the area of **all** peaks eluting within the Rt windows specified for these ranges, excluding surrogates, as described below in Sections 9.9.2.1 and 9.9.2.2.

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

9.9.2.1 C_9-C_{18} Aliphatic Hydrocarbons and C_{19}-C_{36} Aliphatic Hydrocarbons

- Sum all peaks in the appropriate Rt window, as specified in Section 9.6 and Table 6 (using baseline integration).
- From this sum, subtract the area counts of any surrogates which elute in this range (using valley-to-valley integration).
- Equations 8 and 9 are used to calculate the concentrations of C_9-C_{18} aliphatic hydrocarbons and C_{19}-C_{36} aliphatic hydrocarbons in aqueous and non-aqueous samples, respectively.

Equation 8: Aqueous Samples (Hydrocarbon Ranges and TPH)

$$\text{Conc HC Range or TPH } (\mu g/L) = \frac{(A_x)(D)(V_t)}{(\text{Range CF})(V_s)}$$

where:

Ax =	Area count for hydrocarbon range of interest
D =	Dilution factor (see Section 9.8.10)
Range CF =	Average CF for hydrocarbon range
V_t =	Volume of total extract, µL (including fractionation surrogate volume)
V_s =	Volume of sample extracted, mL.

Equation 9: Non-Aqueous Samples (Hydrocarbon Ranges and TPH)

$$\text{Conc HC Range or TPH (ug/kg)} = \frac{(A_x)(V_t)(D)}{(W_d)(\text{Range CF})}$$

where:

W_d = Dry weight of sample, g (see Equations 10 through 12)
A_x, V_t, D, and Range CF have the same definition as described above for Equations 8 and 9.

9.9.2.2 C_{11}-C_{22} Aromatic Hydrocarbons

- Sum all peaks in the appropriate Rt window, as specified in Section 9.6 and Table 6 (using baseline integration).

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

- Calculate the concentrations in aqueous and non-aqueous samples using Equations 8 and 9, respectively.

  NOTE: These values are reported as the "Unadjusted C_{11}-C_{22} aromatics" as shown in Appendix 3, Exhibit 1.

- From the Unadjusted concentration (µg/L or µg/kg), calculate the concentration of C_{11}-C_{22} aromatic hydrocarbons by subtracting the concentrations of the Target PAH Analytes (which are quantified using the FID or GC/MS). This is the final concentration reported as the "C_{11}-C_{22} Aromatic Hydrocarbons" on the data report form in Appendix 3, Exhibit 1.

9.9.3 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample extracted (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.4. Using the data obtained from Section 9.4, W_d is calculated using Equations 10 through 12.

Equation 10: Percent Moisture

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

Equation 11: Percent Solids

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

Equation 12: Dry Weight of Sample

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

9.10 Determination of Target PAH Analytes and EPH Aliphatic and Aromatic Hydrocarbon Range Concentrations by Gas Chromatography/Mass Spectrometry (GC/MS)

Target PAH Analytes may be quantified from a fractionated or unfractionated extract using GC/MS and must satisfy the requirements listed below. Aliphatic and aromatic hydrocarbon ranges may only be quantified **after fractionation** using GC/MS under the MassDEP EPH Method and not be considered a "Significant Modification", as described in Section 11.3.1.1, by satisfying the following requirements:

9.10.1 Target PAH Analytes in the aromatic hydrocarbon range must be identified, quantified and satisfy the QC requirements and performance standards of SW-846 Method 8270E as described in WSC-CAM-II B with the modifications listed below. For quantification of the EPH aliphatic and aromatic ranges, the MS detector must be operated in the Total Ion Current mode.

9.10.2 Modified SW-846 Method 8270E QC Requirements for EPH Analysis*

* All referenced Section numbers refer to SW-846 Method 8270E.

9.10.2.1 DFTPP must be used as a tuning standard (Section 7.6).

9.10.2.2 5-alpha-androstane (using m/z 245 as primary quantitation ion) is the recommended internal standard; other internal standards may be used, as appropriate.

9.10.2.3 OTP is the recommended analytical surrogate to evaluate %R of the Target PAH analytes contained in the aromatic fraction; other surrogates (i.e., d_8-Naphthalene) may be used, as appropriate.

9.10.2.4 Evaluation of DDT breakdown, and pentachlorophenol and benzidine tailing is not required (Section 11.3.1.3).

9.10.2.5 All Target PAH Analytes described in Table 2 must meet the initial and continuing calibration requirements for the SW-846 Method 8270E described in WSC-CAM-II B unless specifically excepted in this section.

9.10.2.6 Hydrocarbon range response factors must be based on all individual aliphatic or aromatic calibration standards described in Tables 1 and 2, that are included within the specified range as defined by the EPH marker compounds described in Table 6. Hydrocarbon range response factors are determined using the summation of the peak areas (Total Ion Current) for all individual calibration standard components that elute within a specified range (i.e., C_9–C_{18} Aliphatic Hydrocarbons, 6 components) and the total concentration injected.

9.10.2.7 All Target PAH Analytes and hydrocarbon ranges must be evaluated in the initial calibration and continuing calibration verifications (CCVs) and meet the performance standards described in Table 7.

9.10.2.8 Evaluation of Continuing Calibration Standards (equivalent to the CCV described in SW-846 Method 8270E) is required at the beginning and end of each analytical sequence.

9.10.2.9 The analytical batch for EPH analyses may include the analysis of up to 20 samples completed within 12 hours of the batch's tune.

9.10.2.10 The performance standards for the EPH aliphatic and aromatic hydrocarbon ranges and comparable performance standards for the Target PAH Analytes are presented in Table 7. In addition to these performance standards, the performance standards for the Target PAH Analytes must also meet the requirements of SW-846 Method 8270E as described in WSC-CAM-II B, Table II B-1.

9.10.3 If the aliphatic hydrocarbon range concentrations are quantified by GC/MS, naphthalene and 2-methylnaphthalene must be identified and quantified in the aliphatic hydrocarbon fraction of each sample using SW-846 Method 8270E, using an internal standard. **If either the concentration of naphthalene or 2-methylnaphthalene in the aliphatic fraction exceeds 5% of the <u>total</u> concentration for naphthalene or 2-methylnaphthalene in the sample, fractionation must be repeated on the archived sample extract. NOTE: The <u>total</u> concentration of naphthalene or 2-methylnaphthalene in the sample includes the summation of the concentration detected in the aliphatic fraction and the concentration detected in the aromatic fraction.**

9.10.4 The QC requirements and performance standards for SW-846 Method 8270E described in WSC-CAM-II B must also be satisfied.

9.10.5 The sample must be extracted using the procedures described in Section 9.1 and the resultant concentrated extract fractionated as described in Section 9.2.

9.10.6 WSC-CAM-II B must be identified as the "Method for Target Analytes" and "Method for Ranges", as applicable, on the Required EPH Data Report Information form described in Appendix 3.

9.10.7 Any other modifications to the WSC-CAM-II B Method must be described in detail in the laboratory narrative.

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 An SSB must be run after all highly contaminated samples to minimize the potential for sample carryover.

10.1.3 Batch Analytical QC Samples

10.1.3.1 At a minimum, for each analytical batch (up to 20 samples) or every 24 hours, whichever comes first, a beginning and ending Continuing Calibration Standard must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range Continuing Calibration Standard should also be considered. However, it should be noted that the analysis of the Continuing Calibration Standard is required prior to sample analysis, after every 20 samples or every 24 hours, whichever comes first, and at the end of an analytical sequence, at a minimum.

10.1.3.2 At a minimum, for each extraction batch (up to 20 samples of similar matrix), an LMB, LCS, and an LCS Duplicate must also be prepared and results analyzed as part of the laboratory's continuing QC program. The blank and QC samples fortified with known concentrations and volumes of analytical standards should be carried through the complete sample preparation and measurement processes.

10.1.4 The recommended sequence of analysis is as follows:

(1) Analytical batch Calibration Standards (initial) or mid-range Continuing Calibration Standard (daily check of initial calibration). **[REQUIRED]**
(2) Initial Calibration Verification. **[REQUIRED only after initial calibration]**
(3) Extraction batch LCS. **[REQUIRED]**
(4) Extraction batch LCS Duplicate. **[REQUIRED]**
(5) Extraction batch LMB. **[REQUIRED]**
(6) Batch samples. (up to 20 samples or 24 hours, whichever comes first)
(7) Matrix duplicate. [**As requested by data user**]
(8) Matrix Spike/Matrix Spike Duplicate. [**As requested by data user**]
(9) Optional mid-range Continuing Calibration Standard. (consider after 10 samples)
(10) Closing mid-range Continuing Calibration Standard[a] after 20 samples or 24 hours, whichever comes first, and at end of analytical batch. **[REQUIRED]**

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

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

10.2 Minimum Instrument QC

10.2.1 The instrument must be able to achieve adequate separation and resolution of peaks and analytes of interest.

10.2.1.1 The n-nonane (n-C_9) peak must be adequately resolved from the solvent front of the chromatographic run.

10.2.1.2 The surrogates COD and OTP must be adequately resolved from any individual components in the Aliphatic Hydrocarbon and Aromatic Hydrocarbon standards.

10.2.1.3 All peaks of interest in the Aliphatic Hydrocarbon standard must be adequately resolved to baseline. In the Aromatic Hydrocarbon standard, baseline separation is expected for phenanthrene and anthracene. Benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene are not expected to be chromatographically separated to baseline and may be reported as an un-resolved mixture, unless adequate resolution is obtained.

10.2.1.4 Due care must be exercised to assure that the peaks for naphthalene and n-dodecane in the aliphatic hydrocarbon fraction are adequately resolved to allow for an accurate determination of the naphthalene concentration in the LCS/LCSD pair.

Note: For the purposes of this method, adequate resolution is assumed to be achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks.

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

10.2.3 **System Solvent Blank:** If baseline correction will be employed, as specified in Section 11.2.5, a SSB, air blank, and/or system run must be undertaken with every batch, and after the analysis of a sample that is suspected to be highly contaminated. Baseline correction for EPH aliphatic and aromatic hydrocarbon area data may not be used for any sample for which the area count associated with the baseline correction is greater than 10% of the uncorrected area count for the sample's corresponding collective range. For purposes of this analytical requirement, any sample with an on-column concentration greater than the highest calibration standard is considered "highly contaminated" (see Section 4.3).

10.2.4 **Laboratory Method Blank:** A water or soil LMB is prepared by fortifying a reagent water blank (for aqueous samples) or clean sand blank (for soil/sediment samples) with the surrogate spiking solution (using the same volume of surrogate as samples). Peaks must not be detected above the RL within the Rt 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 standards for aqueous samples. Peaks detected within the Rt window of any analyte or range of interest above the RL must be noted on the data report form. Re-extraction of all associated samples may be warranted

10.2.5 **Retention Times Windows:** must be established for each Target PAH Analyte and hydrocarbon range of interest each time a new GC column is installed and must be verified and/or adjusted on a daily basis. (See Sections 9.6 and 9.7.5).

10.2.6 **Calibration**

10.2.6.1 **Initial Calibration**: CFs must be calculated for each Target PAH Analyte, surrogate, and hydrocarbon range based upon the analysis of a minimum of 5 calibration standards. The linearity of CFs may be assumed if the %RSD over the working range of the calibration curve is $\leq$25. (See Section 9.7.2). For linear regression, r must be $\geq$0.99.

10.2.6.2 **Continuing Calibration Standard**: The Continuing Calibration Standard must be analyzed daily prior to sample analysis, every 20 samples or every 24 hours (whichever comes first), and at the end of an analytical sequence to verify the accuracy of the calibration of the instrument. For Target PAH Analytes, surrogates, and hydrocarbon

ranges, the %D or Percent Drift must be ≤25. If more than one Target PAH Analyte or hydrocarbon range fails to meet this criterion, the instrument must be recalibrated. Otherwise, sample analysis may proceed. For the closing continuing calibration standard (analyzed after every 20 samples, every 24 hours, or at end of analytical sequence), four compounds may exhibit %Ds or Percent Drifts greater than 25% but less than 40%.

10.2.7 **Laboratory Control Sample:** An LCS is prepared by fortifying a reagent water blank (for aqueous samples) or clean sand blank (for soil/sediment samples) with the matrix spiking solution. The spike recoveries for the Target PAH Analytes and the hydrocarbon ranges must be between 40% and 140%.

- If the recoveries are low and outside of the acceptance limits, re-extract and 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, re-extract and 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.

10.2.8 **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 relative percent difference (RPD) of the concentrations (not recoveries) of the LCS/LCSD pair. The RPD for Target PAH Analytes and aliphatic and aromatic hydrocarbon range concentrations must be ≤25. See Section 10.2.7 for corrective actions associated with recoveries outside of acceptance limits.

10.2.9 **Surrogate Spike Recoveries**

Each sample, LMB, LCS, LCSD, matrix spike, and matrix duplicate must be fortified with the surrogate spiking solution. Required surrogate recovery is 40% to 140%. At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 40% or more than 140%, 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, reextract and reanalyze the sample if the recovery of one surrogate is less than 40% or the recoveries of both surrogates are outside the acceptance limits. The laboratory may first reanalyze the archived portion (prior to fractionation) to see if the surrogate recoveries were possibly affected by fractionation. If surrogate recoveries are acceptable in the archived portion, refractionation and reanalysis of the archived extract must be performed. Reextraction and reanalysis are not required if one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture); and
(2) The surrogate exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in the sample.

If a sample with a surrogate recovery outside of the acceptable range is not reextracted or 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.

10.2.10 In order to demonstrate the absence of aliphatic mass discrimination, the response ratio of C_{28} to C_{20} must be at least 0.85. If <0.85, this nonconformance must be noted in the laboratory narrative. The chromatograms of Continuing Calibration Standards for aromatics must be reviewed to ensure that there are no obvious signs of mass discrimination.

10.2.11 Each sample (field and QC sample) must be evaluated for potential breakthrough on a sample-specific basis by evaluating the %R of the fractionation surrogate (2-bromonaphthalene) and on a batch basis by quantifying naphthalene and 2-methylnaphthalene in both the aliphatic and aromatic fractions of the LCS and LCSD. **If either the concentration of naphthalene or 2-methylnaphthalene in the aliphatic fraction exceeds 5% of the total concentration for naphthalene or 2-methylnaphthalene in the LCS or LCSD, fractionation must be repeated on all archived batch extracts.** If the fractionation surrogate recovery is outside the 40 – 140% limits, then fractionation must be repeated on the archived extract of the affected sample. **NOTE: The total concentration of naphthalene or 2-methylnaphthalene in the LCS/LCSD pair includes the summation of the concentration detected in the aliphatic fraction and the concentration detected in the aromatic fraction.**

Analytical Note: Due care must be exercised to assure that the peaks for naphthalene and n-dodecane in the aliphatic hydrocarbon fraction are adequately resolved to allow for an accurate determination of the naphthalene concentration in the LCS/LCSD pair.

Example Naphthalene* % Breakthrough Calculation

Naphthalene in Aromatic Fraction (N_{ar}): 48 µg/L

Naphthalene in Aliphatic Fraction (N_{al}): 1.5 µg/L

Total Naphthalene Concentration (NT_r): 49.5 µg/L

$$\% \text{ Naphthalene Breakthrough} = \frac{N_{al}}{NT_r} \times 100$$

$$\% \text{ Naphthalene Breakthrough} = \frac{1.5}{49.5} \times 100$$

% Naphthalene Breakthrough = 3.0

* may be applied to 2-methylnaphthalene breakthrough calculation also

10.2.12 **Fractionation Check Solution:** A fractionation check solution is prepared containing 14 alkanes and 17 PAHs at a nominal concentration of 200 ng/µl of each constituent. The Fractionation Check Solution must be used to evaluate the fractionation efficiency of each new lot of silica gel / cartridges as described in Appendix 5, Section 5.0, and establish the optimum hexane volume required to efficiently elute aliphatic hydrocarbons while not allowing significant aromatic hydrocarbon breakthrough. For each analyte contained in the fractionation check solution, excluding n-nonane, the %R (see Appendix 5, Equation 5-4) must be between 40 and 140%. A recovery of 30% is acceptable for n-nonane.

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 extracting and 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 13 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 ≤ 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 13. 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 or soil/sediment sample with a specified volume 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 the background concentrations. The corrected concentrations of the Target PAH Analytes and the hydrocarbon ranges within the matrix spiking sample must be within 40 - 140% of the true value. RPDs between MS and MSD results must be ≤50.

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 re-extracted and/or re-analyzed, as noted in Section 10.2. These QC samples include the opening and closing Continuing Calibration Standards, LMB, LCS, and LCSD. If this is not possible, that data must be reported as suspect.

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

The QC procedures described in Appendix 5 and described in SW-846 Method 8000D, Section 9.3 must be conducted, successfully completed and documented as an IDLC, prior to the analysis of any samples by the EPH 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 5, Section 2.0 (Optional);
- Initial Demonstration of Accuracy, see Appendix 5, Section 3.0;
- Initial Demonstration of Precision, see Appendix 5, Section 4.0;
- Initial Demonstration of Fractionation Efficiency, see Appendix 5, Section 5.0; and
- Method Detection Limit (MDL) Determination, see Appendix 5, Section 6.0 (Optional).

11.0 DATA PRODUCTION AND REPORTING

11.1 Calibration

Using the external standard calibration procedure (9.7.2) calibrate the GC as follows:

11.1.1 Calculate an average CF or linear regression calibration curve for each Target PAH Analyte that comprises the Aromatic Hydrocarbon standard. This step is not necessary if the Target or Diesel PAH Analytes will not be individually identified and quantitated by the EPH method (i.e., if unadjusted values only will be reported for the C_{11}- C_{22} aromatic hydrocarbon range or TPH or if reporting concentrations of Target PAH Analytes via another method).

11.1.2 Calculate an average CF or linear regression calibration curve for the surrogates OTP, COD, and the fractionation surrogates.

11.1.3 Calculate an average collective CF or linear regression calibration curve for the total concentration of the C_9-C_{18} Aliphatic Hydrocarbons. Tabulate the collective peak area response of the 6 components against the collective concentration injected. Do not include the area responses of the internal standard, naphthalene, and 2-methylnaphthalene.

11.1.4 Calculate an average CF or linear regression calibration curve for naphthalene and 2-methylnaphthalene from the Aliphatic Hydrocarbon standard. This is not required if the same instrument is calibrated, separately, for all aliphatic and aromatic compounds using the same internal standard and resolution of naphthalene from n-C_{12} is demonstrated.

11.1.5 Calculate an average collective CF or linear regression calibration curve for the total concentration of the C_{19}-C_{36} Aliphatic Hydrocarbons. Tabulate the collective peak area response of the 8 components against the collective concentration injected. Do not include the area response of the surrogate COD.

11.1.6 Calculate an average collective CF or linear regression calibration curve for the total concentration of the C_{11}-C_{22} Aromatic Hydrocarbons. Tabulate the collective peak area response of the 17 components against the collective concentration injected. Do not include the area responses of the surrogates OTP, 2-bromonaphthalene, or 2-fluorobiphenyl.

11.1.7 For TPH analyses without fractionation, calculate an average collective CF or linear regression calibration curve. Tabulate the collective peak area response of the 14 aliphatic components against the collective concentration injected. Do not include the area responses of surrogates or naphthalene and 2-methylnaphthalene in the Aliphatic Hydrocarbon standard.

11.2 Sample Analysis

11.2.1 Aliphatic Fraction

11.2.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the Rt for n-C_9 and 0.1 minutes before the Rt for n-C_{19}. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.1.2 Determine the total area count for all peaks eluting 0.1 minutes before the Rt for n-C_{19} and 0.1 minutes after the Rt for n-C_{36}. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.1.3 Determine the peak area count for the extraction surrogate COD. Subtract this value from the collective area count value within the C_{19} through C_{36} aliphatic hydrocarbon range.

11.2.1.4 Using the equations contained in Section 9.9, calculate the concentrations of C_9 through C_{18} Aliphatic Hydrocarbons, C_{19} through C_{36} Aliphatic Hydrocarbons, and the surrogate COD.

11.2.2 Aromatic Fraction

11.2.2.1 Determine the total area count for all peaks eluting 0.1 minutes before the Rt for naphthalene and 0.1 minutes after the Rt for benzo(g,h,i)perylene.

11.2.2.2 Determine the peak area count for the extraction surrogate OTP and fractionation surrogate(s). Subtract these values from the collective area count value.

11.2.2.3 Optionally, determine the peak area count for the individual Target or Diesel PAH Analytes.

11.2.2.4 Using the equations contained in Section 9.9, calculate the concentrations of Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons, the surrogate standard OTP, fractionation surrogate standard(s) and optionally, the Target or Diesel PAH Analytes.

11.2.3 Total Petroleum Hydrocarbons

11.2.3.1 Determine the total area count for all peaks eluting 0.1 minutes before the Rt for n-C_9 and 0.1 minutes after the Rt for n-C_{36}. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.3.2 Determine the peak area count for any surrogate and internal standards used. Subtract these values from the collective area count value.

11.2.3.3 Using the equations contained in Section 9.9, calculate the concentration of Unadjusted TPH.

11.2.4 Data Adjustments

11.2.4.1 By definition, the collective concentration of the aromatic fraction (and/or TPH) **excludes** the individual concentrations of the Target PAH Analytes. Accordingly, a data adjustment step is necessary to adjust the collective hydrocarbon range concentration calculated in Sections 11.2.2.4 and 11.2.3.3 to eliminate "double counting" of analytes.

11.2.4.2 The necessary data adjustment step may be taken by the laboratory reporting the hydrocarbon range/TPH concentration data, or by the data user. The extent of data adjustments taken by the laboratory must be noted on the data report form.

11.2.4.3 Subtract the individual concentrations of the Target or Diesel PAH Analytes from the collective concentration of Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons. Do not subtract any Target or Diesel PAH Analyte concentration if this concentration is less than the RL. If the individual concentrations of Target PAH Analytes have been quantified using another method (e.g., by using an MS detector), note this on the data report form. It should be noted that the reported Target PAH Analyte results must be the results used to adjust the C_{11}-C_{22} Aromatic Hydrocarbon results. If the individual concentrations of Target PAH Analytes have not been quantitated, report the value as Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons, and indicate "Not Determined" for C_{11} through C_{22} Aromatic Hydrocarbons.

11.2.4.4 Subtract the individual concentrations of the Target or Diesel PAH Analytes from the collective concentration of Unadjusted TPH only if the concentrations of the Target or Diesel PAH Analytes were determined using a GC/MS method. If the concentration of Target or Diesel PAH Analytes were not determined using a GC/MS method, report a value for Unadjusted TPH, and indicate "Not Determined" for TPH.

11.2.4.5 For purposes of compliance with the reporting and cleanup standards specified in the MCP, the concentration of Unadjusted C_{11} through C_{22} Aromatic Hydrocarbons and/or Unadjusted TPH may be conservatively deemed to be equivalent to the concentration of C_{11} through C_{22} Aromatic Hydrocarbons and/or TPH.

11.2.5 Baseline Correction for Instrument Noise Level

11.2.5.1 EPH aliphatic and aromatic hydrocarbon range area data determined by the collective integration of all eluting peaks between the specified EPH range marker compounds (see Table 6) may be corrected by the manual or automatic subtraction of the baseline established by the injection of a SSB. Correction in this manner is not recommended or preferred, but is permissible in cases where all reasonable steps have been taken to eliminate or minimize excessive baseline bias associated with analytical system noise.

11.2.5.2 The instrument baseline must be established by the direct injection of a SSB. The injection of an air blank or activation of a temperature programmed chromatographic run without the injection of any material should be used to verify that the system noise is not attributable to solvent contamination. All system operational elements and parameters must be identical to those of a typical sample run.

If baseline correction is used, the baseline must be re-established for every analytical batch by the analysis of a SSB. Baseline correction for EPH aliphatic and aromatic hydrocarbon area data may not be used for any sample for which the area count associated with the baseline correction is greater than 10% of the uncorrected area count for the sample's corresponding collective range.

11.2.6 Contamination of SPE Cartridges

11.2.6.1 Hydrocarbon range integration areas may be affected by peaks identified during the injection of a LMB, and determined to be attributable to the leaching of plasticizers or other contaminants from silica gel SPE cartridges. In general, this contamination affects the C_{11}-C_{22} Aromatic Hydrocarbons. Blank correction is not permissible.

11.2.6.2 The laboratory must report the presence of this contamination in the associated range. Optionally, the laboratory may perform GC/MS analysis of the LMB extract to demonstrate that the contaminant in question is not a C_{11}-C_{22} aromatic hydrocarbon compound. Analysis of only the LMB is acceptable as long as the associated samples exhibit the same contaminant peak at the same Rt. If demonstrated not to be a C_{11}-C_{22} aromatic hydrocarbon compound, the contaminant does not need to be included in the calculation of the C_{11}-C_{22} aromatic hydrocarbon range concentration. The laboratory must provide a discussion in the laboratory narrative if this approach is used.

11.3 Data Reporting Content

11.3.1 The required content for EPH Method data is presented in Appendix 3. This information provides data users with a succinct and complete summary of pertinent information and data, as well as a clear affirmation that the QC procedures and standards specified in this method were evaluated and achieved. Any significant modification to the MassDEP EPH Method, as described in Section 11.3.1.1, and indicated by a negative response to Question E on the MassDEP Analytical Protocol Certification Form (also included in Appendix 3) precludes the affected data from achieving "Presumptive Certainty" status. If a significant modification to the EPH Method is utilized, an attachment to the analytical report must be included to demonstrate compliance with the method performance requirements of Section 1.13 on a matrix- and petroleum product-specific basis.

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

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

11.3.1.1.1 The use of other than a silica-gel fractionation technique;

11.3.1.1.2 The use of an extraction procedure other than those presented in Table 5;

11.3.1.1.3 The use of solvents other than those recommended in this method or approved extraction methods listed in Table 5;

11.3.1.1.4 The use of a detector other than an FID to quantitate range/TPH concentrations (See Notes 1 and 2 below);

11.3.1.1.5 The use of aliphatic or aromatic surrogate compounds with Rts not within ± 2 minutes of the Rts of the recommended compounds or the use of inappropriate surrogates to represent the aliphatic and aromatic ranges;

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

11.3.1.1.7 Failure to provide all of the data and information presented in Appendix 3 as well as the required method deliverables discussed in Section 11.3.2.

NOTE 1: Use of a GC/MS detector operated in the Total Ion Current mode to quantify the EPH Method's aliphatic and aromatic hydrocarbon ranges is not considered a significant modification provided that (1) the sample extract has been fractionated; (2) the GC/MS system was also used to identify and quantify the Target PAH Analytes in the sample's aromatic fraction; and (3) the QC requirements and performance standards specified in Section 9.10 are satisfied.

NOTE 2: If alternate detectors are used with or without fractionation, other than noted above, the laboratory must demonstrate that the performance standards listed in Section 1.13 were achieved. Use of an alternate detector, other than noted above, is considered a "significant modification". Any EPH data produced using a "significant modification" cannot achieve Presumptive Certainty status.

11.3.1.2 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.

11.3.2 In addition to sample results, the EPH 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)
- Fractionation check standard results
- Surrogate spike recoveries (for all field samples and QC samples), including fractionation and extraction surrogates
- Percentage of total naphthalene and 2-methylnaphthalene concentrations detected in the aliphatic fractions of the LCS and LCS Duplicate (see Section 10.2.11)
- Percentage of total naphthalene and 2-methylnaphthalene concentrations detected in the aliphatic fractions of samples when GC/MS is utilized (see Section 9.10.3)
- Results of reanalyses or dilutions, reported as follows:
    - If reextraction or reanalysis due to surrogate issues yields similar non-conformances, the laboratory must report results of both analyses.
    - If rextraction or reanalysis due to surrogate issues is performed outside of holding time and yields acceptable surrogate recoveries, the laboratory must report results of both analyses.
    - If sample is not reanalyzed or reextracted for surrogate issues due to obvious interference, the laboratory must provide the chromatogram in the data report.
    - 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.

- Demonstration of compliance with analytical performance standards specified in Section 1.13 on a matrix- and petroleum product-specific basis (only if a "significant modification" is utilized)

11.3.3 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 3 of this method.

12.0 REPORTING LIMITS

The RLs for Target PAH 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. **Target PAH Analytes with calculated concentrations below the RL should be reported as < the specific Target Analyte's RL (i.e., < 2.0 ug/L).** For GC/MS analysis only, calculated concentrations of Target PAH Analytes below the RL (lowest calibration standard) may be reported as a "J Value", or equivalent.

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 range RL will be set at 50x the concentration of the lowest calibration standard for the associated analyte. Calculated collective concentrations for EPH aliphatic and aromatic hydrocarbon ranges below the RL should be reported as < Range RL (i.e., < 100 ug/L).

Based on the on-column concentration of 1 ηg/µL 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 based on the extraction of 1 liter of sample, a final fractionation extract volume of 2 mL, and a sample injection volume of 1 µL.

Soil/Sediment Samples: Hydrocarbon range RLs would be equivalent to 10 mg/kg (dry weight basis) based on the extraction of 10 grams of soil, a final fractionation extract volume of 2 mL, and a sample injection volume of 1 µL.

13.0 METHOD PERFORMANCE

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-4 in Appendix 1. Chromatograms are provided in Appendix 2.

14.0 REFERENCES

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

2. 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.

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

4. 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.

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

6. USEPA, *Measurements of Petroleum Hydrocarbons: Report on Activities to Develop a Manual*; Prepared by Midwest Research Institute, Falls Church, VA under EPA Contract No. 68-WO-0015, WA No. 4; Submitted to USEPA Office of Underground Storage Tanks; Washington, DC; November 20, 1990.

7. USEPA UST Workgroup, Draft *Method for Determination of Diesel Range Organics*, November, 1990.

8. USEPA Federal Register 40 CFR Part 136, Appendix B, *Guidelines Establishing Test Procedures for the Analysis of Pollutants*, July 1992.

9. USEPA, *Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring*, EPA 821-B-93-001; U.S. Government Printing Office, Washington D.C., June, 1993.

10. USEPA: SW-846 Test Methods for Evaluating Solid Waste, 3rd Edition; Methods 3510C, 3520C, 3540C, 3541, 3545A, 3546, 3580A, 3630C, 8000D, 8100, and 8270E.

11. Wisconsin DNR, *Modified DRO Method for Determining Diesel Range Organics*, PUBL-SW-141, 1992.

TABLES

Table 1. Aliphatic Hydrocarbon Standard

Carbon Number	Compound	Retention Time (min.)[1]
9	n-Nonane	3.14
10	n-Decane	4.55
12	n-Dodecane	7.86
14	n-Tetradecane	11.10
16	n-Hexadecane	14.05
18	n-Octadecane	16.71
19	n-Nonadecane	17.95
20	n-Eicosane	19.14
NA	1-Chloro-octadecane (surrogate)	20.13
22	n-Docosane	21.35
24	n-Tetracosane	23.40
26	n-Hexacosane	25.29
28	n-Octacosane	27.04
30	n-Triacontane	28.69
36	n-Hexatriacontane	34.82

[1]Results obtained using the column and chromatographic conditions described in Sections 6.1 and 9.5, respectively.
NA = Not applicable

Table 2. Aromatic Hydrocarbon Standard/Target PAH Analytes

Compound	Retention Time (min.)[1]
Naphthalene	7.66
2-Methylnaphthalene	9.49
Acenaphthylene	11.93
Acenaphthene	12.46
Fluorene	13.89
Phenanthrene	16.54
Anthracene	16.66
Ortho-Terphenyl (surrogate)	17.95
Fluoranthene	19.92
Pyrene	20.51
Benzo(a)anthracene	24.08
Chrysene	24.21
Benzo(b)fluoranthene	26.94
Benzo(k)fluoranthene	27.02
Benzo(a)pyrene	27.66
Indeno(1,2,3-cd)pyrene[2]	30.25
Dibenz(a,h)anthracene[2]	30.36
Benzo(g,h,i)perylene	30.76

[1]Results obtained using the column and chromatographic conditions described in Sections 6.1 and 9.5, respectively.

[2] Indeno(1,2,3-cd)pyrene and Dibenz(a,h)anthracene may co-elute under the column and chromatographic conditions described in Sections 6.1 and 9.5, respectively.

Table 3. Recommended Calibration Standard Concentrations (1 µL Injection)

	Conc. of standard analytes (ng/µL)				
Concentration of Individual Target PAH Analytes	1	10	50	100	200
Total Concentration C_9 - C_{18} Aliphatic Hydrocarbons (6 components)*	6	60	300	600	1200
Total Concentration C_{19} - C_{36} Aliphatic Hydrocarbons (8 components)*	8	80	400	800	1600
Total Concentration C_{11} - C_{22} Aromatic Hydrocarbons (17 components)	17	170	850	1700	3400
*Assumes concentration of individual aliphatic components equivalent to concentration of individual Target PAH Analytes.					

Table 4. Holding Times and Preservatives for EPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples	1-Liter amber glass bottle with Teflon-lined screw cap	Add 5 mL of 1:1 HCl to pH <2; cool to 0-6° C	Samples must be extracted within 14 days and extracts must be analyzed within 40 days of extraction.
Soil/Sediment Samples	4-oz. (120-mL) wide-mouth amber glass jar with Teflon-lined screw cap	Cool to 0-6° C	Samples must be extracted within 14 days and extracts must be analyzed within 40 days of extraction.
	4-oz. (120-mL) wide-mouth amber glass jar with Teflon-lined screw cap. Jar should be filled to only 2/3 capacity to avoid breakage if expansion occurs during freezing.	Freeze at - 10°C in the field or in the laboratory[1]	Samples must be extracted within 14 days of thawing and extracts must be analyzed within 40 days of extraction.[2]

[1]Samples processed in the laboratory must be preserved at 0-6° C and frozen within 24 hours of the time of collection. Frozen samples may be held for up to one year prior to analysis and must be extracted within 14 days of thawing.
[2]Once the thawing process begins, samples must be kept at 0-6° C until extraction.

Table 5. Approved EPH Extraction Methods

SW-846 Method	Matrix	Description
3510C	Aqueous	Separatory Funnel Liquid-Liquid Extraction
3520C	Aqueous	Continuous Liquid-Liquid Extraction
3511	Aqueous	Organic Compounds in Water by Microextraction
3535A	Aqueous	Solid Phase Extraction (SPE)
3540C	Soil/Sediment	Soxhlet Extraction
3541	Soil/Sediment	Automated Soxhlet Extraction
3545A	Soil/Sediment	Pressurized Fluid Extraction (PFE)
3546	Soil/Sediment	Microwave Extraction
3570	Soil/Sediment	Microscale Solvent Extraction (MSE)
3550C	Contaminated Solids[1]	Ultrasonic Extraction
3580A	NAPL	Waste Dilution
[1]Ultrasonic extraction may only be used for the extraction of highly contaminated (free product) non-soil/sediments (debris). Any other use of ultrasonic extraction is considered a **"significant modification"** of the EPH Method.		

Table 6. EPH Marker Compounds

Hydrocarbon Range	Beginning Marker	Ending Marker
C_9-C_{18} Aliphatic Hydrocarbons	0.1 min before n-Nonane	0.1 min before n-Nonadecane
C_{19}-C_{36} Aliphatic Hydrocarbons	0.1 min before n-Nonadecane	0.1 min after n-Hexatriacontane
C_{11}-C_{22} Aromatic Hydrocarbons	0.1 min before Naphthalene	0.1 min after Benzo(g,h,i)perylene

Table 7. Modified SW-846 Method 8270E Analytical QC Requirements and Performance Standards for Target PAH Analyte and EPH Aliphatic and Aromatic Hydrocarbon Range Analyses

QC ELEMENT	PERFORMANCE STANDARD	
	Target PAH Data	EPH Range Data
Initial Calibration (% RSD)	≤ 20	≤ 25
Opening CCV (% drift)	≤ 20	≤ 25
Closing CCV (% drift)	≤ 20	≤ 25
Method Blanks	< RL	< RL
Internal Standard (IS)	Area Count of IS must be within 50 and 200% of associated Opening CCV	Area Count of IS must be within 50 and 200% of associated Opening CCV
Surrogate Recovery	40 – 140%	40 – 140%
Fractionation Surrogate Recovery	Not Required	40 – 140%
Laboratory Control Sample (LCS)	40 –140%	40 –140%
LCS Duplicate (RPD)	≤20 for water, ≤30 for soil/sediment	≤25
Matrix Spike (MS)/MS Duplicate[1]	40 –140%; RPD ≤50	40 –140%; RPD ≤50
LCS/LCSD and Sample Naphthalene or 2-Methylnaphthalene Breakthrough	≤ 5% of total for either constituent in EPH aliphatic fraction[2]	≤ 5% of total for either constituent in EPH aliphatic fraction[2]

1. At discretion of data user
2. Naphthalene and 2-Methylnaphthalene must be measured in EPH aliphatic fraction of each sample for GC/MS analysis. Sample must be re-fractionated if concentration of either compound in the aliphatic fraction is >5% of the total measured in the aliphatic and aromatic extracts.

APPENDIX 1

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMIT (MDL) DATA

Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
C_9	1.79	0.13	72	7.3	0.41
C_{10}	2.65	0.02	106	0.7	0.06
C_{12}	2.46	0.03	98	1.2	0.09
C_{14}	2.51	0.05	100	1.9	0.15
C_{16}	2.54	0.05	102	1.8	0.14
C_{18}	2.53	0.05	101	2.1	0.17
C_{19}	2.52	0.05	101	2.0	0.16
C_{20}	2.50	0.06	100	2.4	0.19
COD	2.39	0.06	96	2.3	0.18
C_{22}	2.45	0.08	98	3.2	0.25
C_{24}	2.41	0.10	96	4.0	0.30
C_{26}	2.40	0.13	96	5.4	0.41
C_{28}	2.43	0.16	97	6.6	0.50
C_{30}	2.46	0.16	98	6.5	0.50
C_{36}	2.63	0.46	105	17.5	1.44

[a] Compounds were spiked into 7 samples at a concentration of 2.5 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into Reagent Water and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (µg/L)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (µg/L)
	Mean	Std. Dev.			
Naphthalene	2.36	0.04	94	1.9	0.14
2-Methylnaphthalene	2.36	0.06	94	2.4	0.18
Acenaphthylene	2.37	0.04	95	1.9	0.14
Acenaphthene	2.39	0.05	96	2.2	0.16
Fluorene	2.35	0.08	94	3.4	0.25
Phenanthrene	2.29	0.10	91	4.3	0.31
Anthracene	2.02	0.10	81	4.8	0.30
OTP	2.36	0.10	94	4.2	0.31
Fluoranthene	2.26	0.15	90	6.6	0.47
Pyrene	2.27	0.15	91	6.6	0.47
Benzo(a)Anthracene	2.27	0.19	91	8.3	0.60
Chrysene	2.30	0.19	92	8.3	0.60
Benzo(b)Fluoranthene	2.47	0.19	99	7.7	0.60
Benzo(k)Fluoranthene	2.49	0.21	99	8.4	0.66
Benzo(a)Pyrene	2.29	0.15	92	6.6	0.50
Indeno(123 cd)Pyrene	2.00	0.13	80	6.5	0.41
Dibenz(ah)Anthracene	1.99	0.14	80	7.0	0.44
Benzo(ghi)Perylene	2.11	0.18	84	8.5	0.57

[a] Compounds were spiked into 7 samples at a concentration of 2.5 µg/L.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.

Table 1-3. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Alkanes Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
C_9	0.49	0.02	98	3.7	0.06
C_{10}	0.46	0.02	92	3.9	0.06
C_{12}	0.44	0.02	88	4.5	0.06
C_{14}	0.46	0.03	92	6.5	0.09
C_{16}	0.48	0.03	96	6.2	0.09
C_{18}	0.51	0.03	102	5.8	0.09
C_{19}	0.52	0.03	104	5.8	0.09
C_{20}	0.53	0.03	106	5.7	0.09
COD	0.53	0.03	106	5.7	0.09
C_{22}	0.55	0.03	110	5.5	0.09
C_{24}	0.56	0.04	112	7.1	0.13
C_{26}	0.57	0.05	114	8.8	0.16
C_{28}	0.57	0.06	114	10.5	0.19
C_{30}	0.58	0.07	116	12.1	0.22
C_{36}	0.62	0.02	124	3.2	0.06

[a] Compounds were spiked into 7 samples at a concentration of 0.5 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.

Table 1-4. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Polynuclear Aromatic Hydrocarbons (PAHs) Spiked Into EPH-Free Sand and Analyzed by the EPH Method

Compound[a]	Compound Conc. Measured (mg/Kg)		Mean Accuracy (Mean % Recovery[b])	Method Precision (RSD[c] - %)	MDL (mg/Kg)
	Mean	Std. Dev.			
Naphthalene	0.48	0.03	96	6.3	0.09
2-Methylnaphthalene	0.48	0.03	96	6.3	0.09
Acenaphthylene	0.50	0.03	100	6.0	0.09
Acenaphthene	0.51	0.03	102	5.9	0.09
Fluorene	0.51	0.03	102	5.9	0.09
Phenanthrene	0.53	0.05	106	9.4	0.16
Anthracene	0.52	0/05	104	9.6	0.16
OTP	0.54	0.04	108	7.4	0.13
Fluoranthene	0.55	0.05	110	9.1	0.16
Pyrene	0.55	0.05	110	9.1	0.16
Benzo(a)Anthracene	0.59	0.06	118	10.2	0.19
Chrysene	0.59	0.06	118	10.2	0.19
Benzo(b)Fluoranthene	0.64	0.06	128	9.3	0.19
Benzo(k)Fluoranthene	0.63	0.05	126	7.9	0.16
Benzo(a)Pyrene	0.62	0.05	124	8.0	0.16
Indeno(123 cd)Pyrene	0.59	0.04	118	6.7	0.13
Dibenz(ah)Anthracene	0.55	0.04	110	7.3	0.13
Benzo(ghi)Perylene	0.58	0.04	116	6.9	0.13

[a] Compounds were spiked into 7 samples at a concentration of 0.5 mg/Kg.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.

APPENDIX 2

CHROMATOGRAMS

Figure 1 Gas Chromatogram (FID) of the EPH Alkane Component Standard (20 µg/L)

Figure 2 Gas Chromatogram (FID) of the EPH PAH Component Standard (20 µg/L)

Figure 3 Gas Chromatogram (FID) of a Diesel Standard (Aliphatic Fractions)

Figure 4 Gas Chromatogram (FID) of a Diesel Standard (Aromatic Fraction)

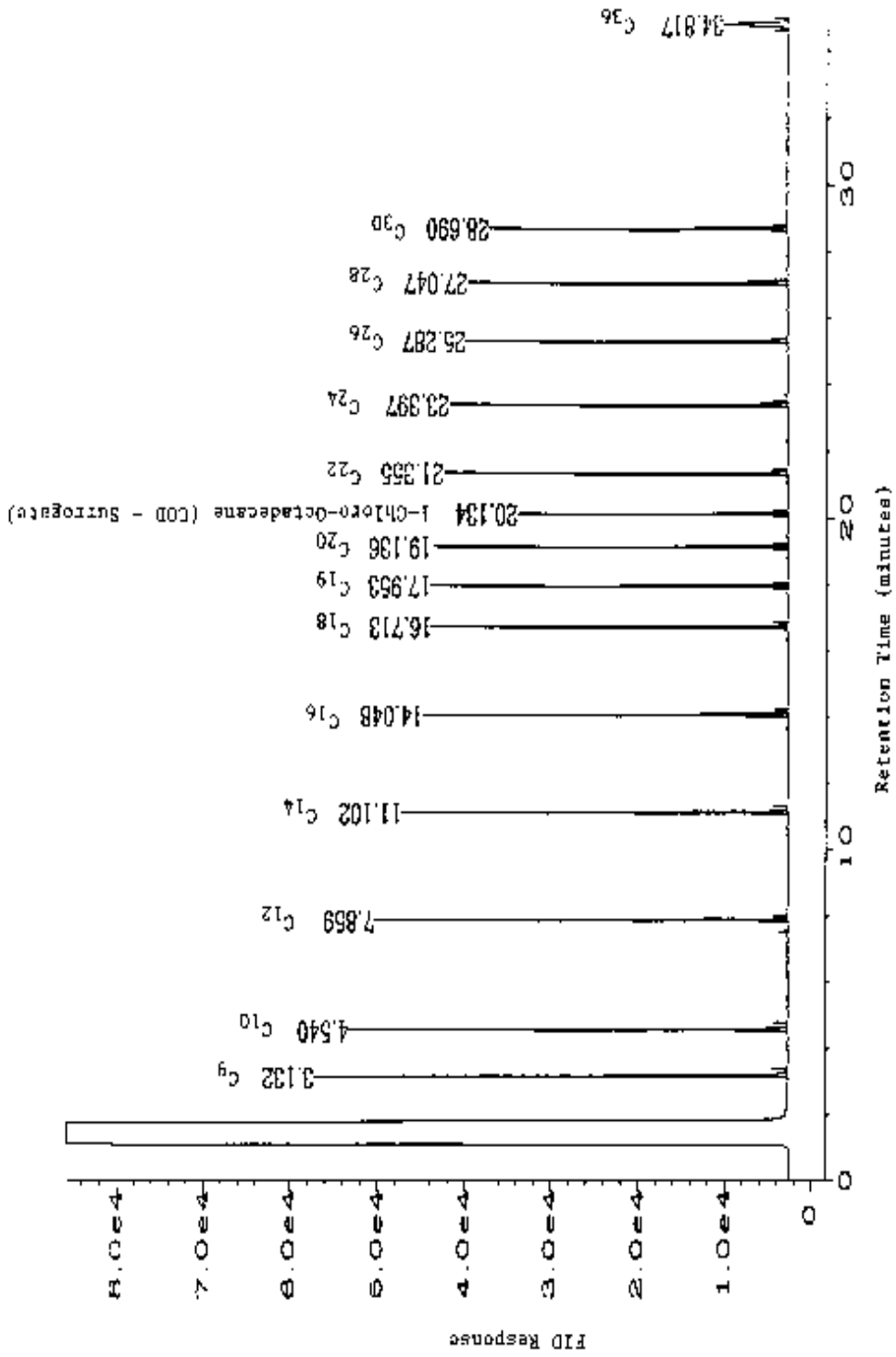

Figure 1. Gas Chromatogram of the Alkane Diesel Component Standard (20 µg/mL).

RTX-5 capillary column (30-m x 0.32-mm i.d., 0.25-µm film thickness); FID at 315°C; splitless injection of 2 µL at 285°C; oven programming, 60°C (hold 1 min) to 290°C at 8°C/min (hold 6.75 min); helium column flow, 2-3 mL/min; helium makeup flow, 30 mL/min; air flow 400 mL/min; hydrogen flow 35 mL/min; electronic pressure control of 15 psi at 60°C.

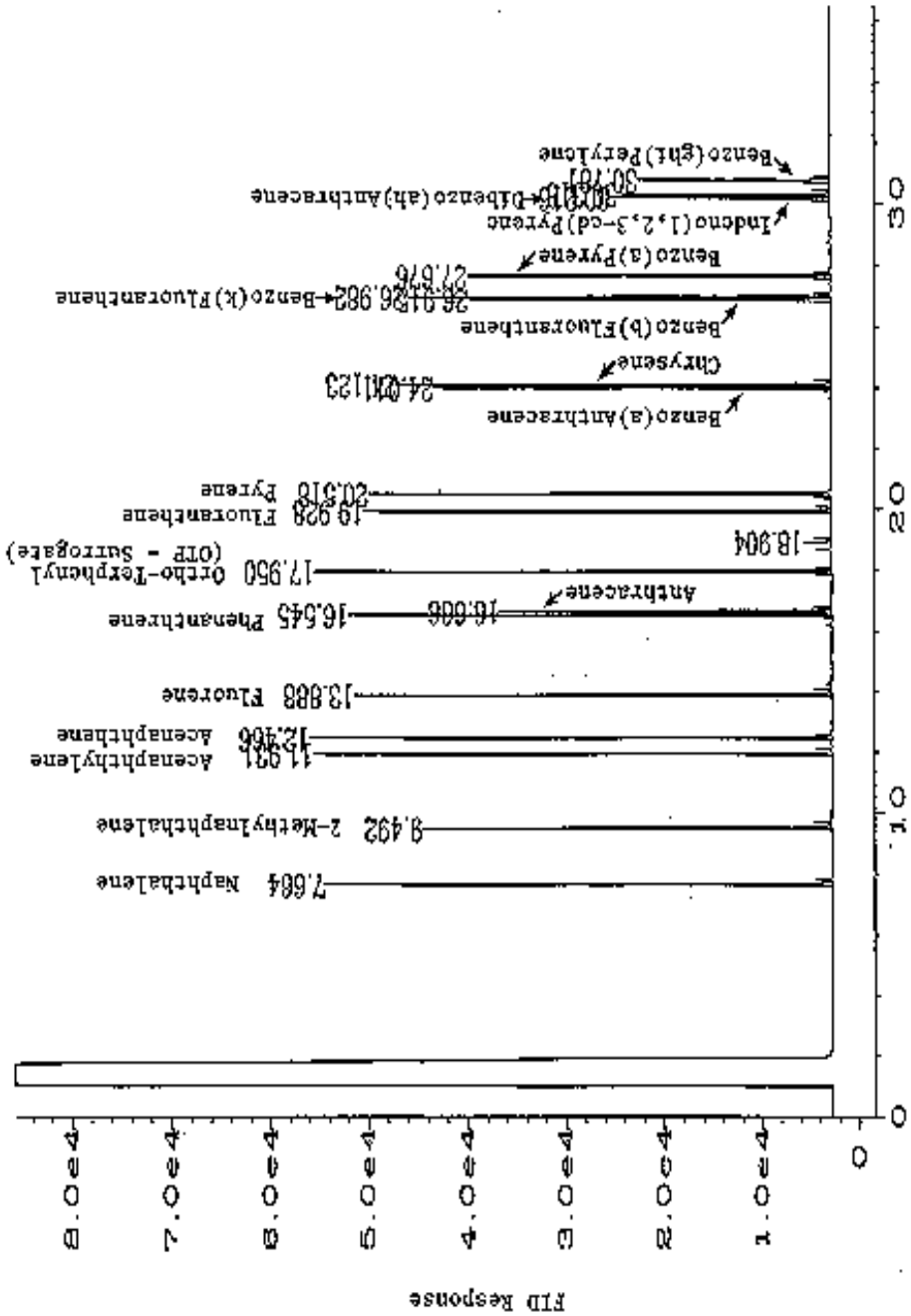

Figure 2. Gas Chromatogram of the PAH Component Standard (20 µg/mL).

All operating conditions same as specified for Figure 1.

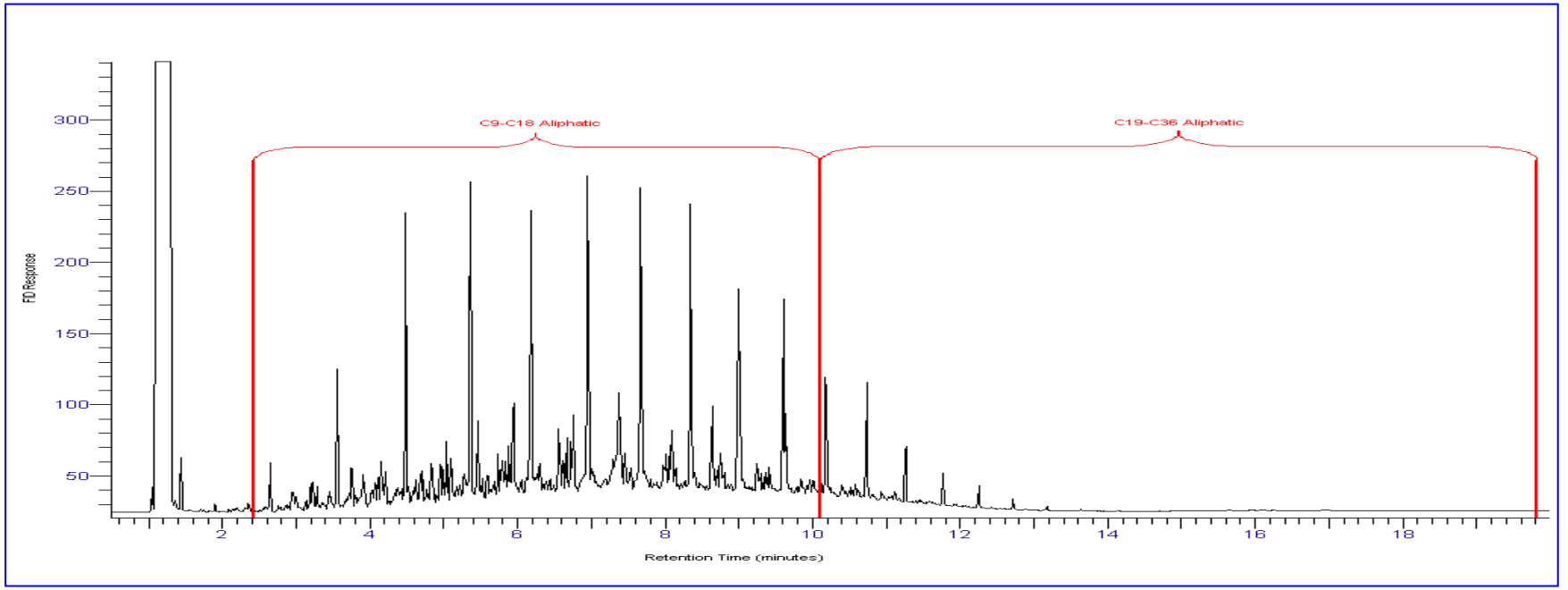

Figure 3 Gas Chromatogram (FID) of a Diesel Standard (Aliphatic Fractions)

Restek RTX-5 SIL-MS capillary column (30 meters, 0.32mm I.D., 0.25 microns film thickness); FID detector on a HP 5890 Series II.

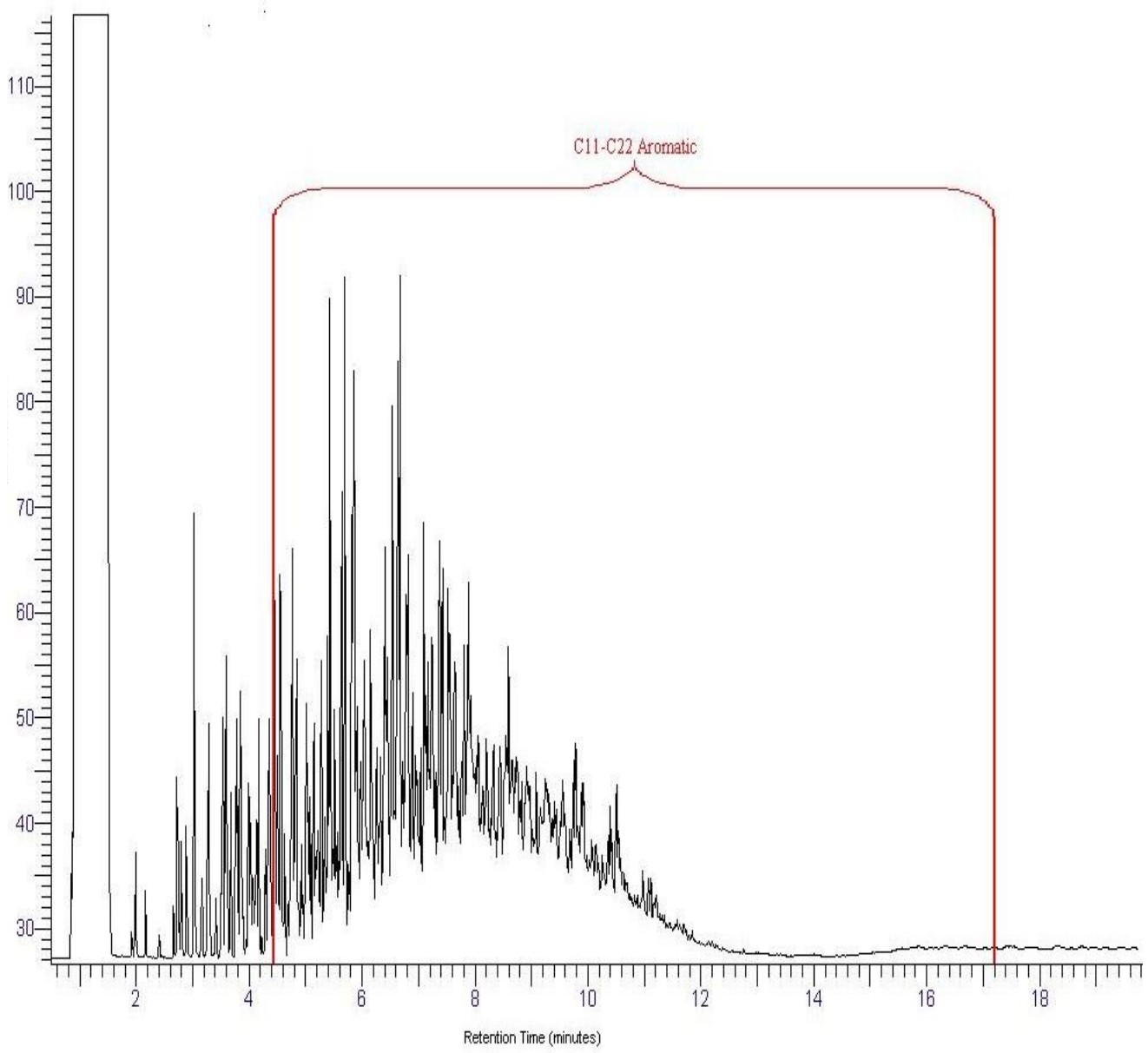

Figure 4 Gas Chromatogram (FID) of a Diesel Standard (Aromatic Fraction)

All operating conditions same as specified on Figure 3

APPENDIX 3

REQUIRED EPH and TPH DATA REPORT INFORMATION

Exhibit 1. Required EPH and TPH Data Report Information

Exhibit 2. MassDEP Analytical Protocol Certification Form

APPENDIX 3
Exhibit 1: Required EPH Data Report Information

SAMPLE INFORMATION

Matrix	☐ Aqueous ☐ Soil ☐ Sediment ☐ Other:
Containers	☐ Satisfactory ☐ Broken ☐ Leaking:
Aqueous Preservatives	☐ N/A ☐ pH≤2 ☐ pH>2 Comment:
Temperature	☐ Received on Ice ☐ Received at 4 ± 2 °C ☐ Other: °C
Extraction Method	Water: Soil/Sediment:

EPH ANALYTICAL RESULTS

Method for Ranges:			**Client ID**					
Method for Target Analytes:			**Lab ID**					
EPH Surrogate Standards:			**Date Collected**					
Aliphatic:			**Date Received**					
Aromatic:			**Date Thawed**					
			Date Extracted					
EPH Fractionation Surrogates:			**Date Analyzed**					
(1)			**Time Analyzed**					
(2)			**Dilution Factor**					
			% Moisture (soil/sediment)					
RANGE/TARGET ANALYTE		**RL**	**Units**					
Unadjusted C11-C22 Aromatics[1]								
Diesel PAH Analytes	**Naphthalene**							
	2-Methylnaphthalene							
	Phenanthrene							
	Acenaphthene							
Other Target PAH Analytes								
C9-C18 Aliphatic Hydrocarbons[1]								
C19-C36 Aliphatic Hydrocarbons[1]								
C11-C22 Aromatic Hydrocarbons[1,2]								
Aliphatic Surrogate % Recovery								
Aromatic Surrogate % Recovery								
Sample Surrogate Acceptance Range				**40-140%**	**40-140%**	**40-140%**	**40-140%**	**40-140%**
Fractionation Surrogate (1) % Recovery								
Fractionation Surrogate (2) % Recovery								
Fractionation Surrogate Acceptance Range				**40-140%**	**40-140%**	**40-140%**	**40-140%**	**40-140%**

[1]Hydrocarbon Range data exclude area counts of any surrogate(s) and/or internal standards eluting in that range
[2]C_{11}-C_{22} Aromatic Hydrocarbons exclude the concentrations of Target PAH Analytes

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APPENDIX 3
Exhibit 1: Required TPH Data Report Information

SAMPLE INFORMATION

Matrix	☐ **Aqueous** ☐ **Soil** ☐ **Sediment** ☐ **Other:**
Containers	☐ **Satisfactory** ☐ **Broken** ☐ **Leaking:**
Aqueous Preservatives	☐ **N/A** ☐ **pH≤2** ☐ **pH>2** **Comment:**
Temperature	☐ **Received on Ice** ☐ **Received at 4 ± 2 °C** ☐ **Other:** **°C**
Extraction Method	**Water:** **Soil/Sediment:**

TPH ANALYTICAL RESULTS

Method for Ranges:			**Client ID**					
Method for Target Analytes:			**Lab ID**					
TPH Surrogate Standards:			**Date Collected**					
			Date Received					
			Date Thawed					
			Date Extracted					
			Date Analyzed					
			Time Analyzed					
			Dilution Factor					
			% Moisture (soil/sediment)					
Range/Target Analyte		**RL**	**Units**					
Unadjusted Total Petroleum Hydrocarbons[1]								
Diesel PAH Analytes	**Naphthalene**							
	2-Methylnaphthalene							
	Phenanthrene							
	Acenaphthene							
Other PAH Target Analytes								
Total Petroleum Hydrocarbons[2]								
Sample Surrogate % Recovery								
Sample Surrogate % Recovery								
Sample Surrogate Acceptance Range				**40-140%**	**40-140%**	**40-140%**	**40-140%**	**40-140%**

[1]Hydrocarbon Range data exclude area counts of any surrogate(s) and/or internal standards eluting in that range
[2]Total Petroleum Hydrocarbons exclude the concentration of PAH Target Analytes only if determined by GC/MS

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APPENDIX 3
Exhibit 2: MassDEP Analytical Protocol Certification Form

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

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

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

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

Signature:_____ **Position:**_____

Printed Name:_____ **Date:**_____

APPENDIX 4

EPH METHOD CALIBRATION AND ANALYSIS USING LINEAR REGRESSION

APPENDIX 4
EPH 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 PAH Analyte and hydrocarbon range concentrations and instrument responses.

1.0 Prepare EPH Calibration Standards as described in Table 3 in the method at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 7.0. The EPH marker compounds for the C_9-C_{18} aliphatic, C_{19}-C_{36} aliphatic and C_{11}-C_{22} aromatic hydrocarbon ranges are presented in Table 6 in the method.

Analyze each EPH Calibration Standard following the procedures outlined in Section 9.7. Tabulate area responses against the injected concentration. These data are used to calculate a calibration curve for each Target PAH Analyte (Equation 4-1). The correlation coefficient (r) of the resultant calibration curve must be ≥0.99.

Equation 4-1: Linear Regression: Target PAH Analytes

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

where:

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

A calibration curve may also be established for each aliphatic and aromatic hydrocarbon range of interest. Calculate the calibration curve for C_9-C_{18} and C_{19}-C_{36} Aliphatic Hydrocarbons and C_{11}-C_{22} Aromatic Hydrocarbons using the FID chromatogram of the appropriate fraction. Tabulate the summation of the peak areas of all components in that hydrocarbon range (i.e., C_9-C_{18} Aliphatic Hydrocarbons, 6 components) against the total concentration injected. These data are used to calculate a calibration curve for each EPH hydrocarbon range (Equation 4-2). The correlation coefficient (r) of the resultant calibration curve must be ≥0.99.

Note: Do not include the area of any surrogates or internal standard when determining the calibration curve for the hydrocarbon ranges. Do not include the area of naphthalene or 2-methylnaphthalene when determining the calibration curve for $C_9 – C_{18}$ Aliphatic Hydrocarbons.

Equation 4-2: Linear Regression: EPH Aliphatic and Aromatic Hydrocarbon Ranges

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

where:

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

2.0 The concentration of a specific Target PAH Analyte or hydrocarbon range in aqueous samples may be calculated using linear regression analysis by applying Equation 4-3.

Equation 4-3: Determination of Target PAH Analytes and Hydrocarbon Range Concentrations in Aqueous Samples using Linear Regression

$$Conc\ Analyte\ or\ HC\ Range(\mu g/L) = \left(\frac{Ax - b}{a}\right) x\ D\ x\ \frac{Vt}{Vs}$$

where:

A_x = Response for the Target PAH Analyte or hydrocarbon range in the sample. Units are in area counts for Target PAH Analytes and the hydrocarbon ranges.
D = Dilution factor; if no dilution was made, D = 1, dimensionless.
a = Slope of the line for Target PAH Analyte or hydrocarbon range.
b = Intercept of the line for Target PAH Analyte or hydrocarbon range.
V_t = Volume of total extract, µL (including fractionation surrogate volume)
V_s = Volume of sample extracted, mL.

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

3.0 The concentration of a specific Target PAH Analyte or hydrocarbon range in a soil/sediment sample may be calculated using linear regression analysis by applying Equation 4-4.

Equation 4-4: Determination of Target PAH Analytes and Hydrocarbon Range Concentrations in Soil/Sediment Samples using Linear Regression

$$Conc\ Analyte\ or\ HC\ Range\ (\mu g/kg) = \left(\frac{Ax - b}{a}\right)\ x\ D\ x\ \frac{(Vt)(D)}{W_d}$$

where: A_x, a, b, V_t, and D have the same definition as for aqueous samples in Equation 4-3, and
W_d = Dry weight of sample, g (see Section 9.9.3)

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

4.0 At a minimum, the working calibration factor must be verified on each working day, after every 20 samples or every 24 hours (whichever comes first), and at the end of the analytical sequence to verify instrument performance and linearity. The Percent Drift is determined using Equation 4-5. The Percent Drift for each Target PAH Analyte, surrogate, and hydrocarbon range must be ≤25. A greater Percent Drift is permissible for n-nonane. If the Percent Drift for n-nonane is >30, note the nonconformance in the laboratory narrative. If more than one Target PAH Analyte or hydrocarbon range fails to meet the criteria, the instrument must be recalibrated. Otherwise, sample analysis may proceed.

For the closing continuing calibration standard (analyzed after every 20 samples, every 24 hours, or at end of analytical sequence), four compounds may exhibit Percent Drifts >25 but <40.

Equation 4-5: Percent Drift

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

APPENDIX 5

INITIAL DEMONSTRATION OF LABORATORY CAPABILITY (IDLC)

FOR THE MassDEP EPH 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 Initial Demonstration of Fractionation Efficiency

6.0 Method Detection Limit (MDL) Determination

Appendix 5
INITIAL DEMONSTRATION OF LABORATORY CAPABILITY (IDLC) for MassDEP EPH Method

For purposes of the IDLC accuracy and precision determinations (***and only this application***) the calibration mixture presented in Tables 1 and 2 of the method is considered to be representative of Extractable Petroleum Hydrocarbon (EPH) Target PAH 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 PAH Analytes and the C_9 through C_{18} aliphatic, C_{19} through C_{36} aliphatic and C_{11} through C_{22} aromatic hydrocarbon 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 EPH Method. A laboratory may not report data to be used in support of MCP decisions unless the IDLC QC requirements and performance standards described below and compiled in Table 5-1 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) must be prepared and treated exactly as a typical field sample submitted for analysis, including fractionation and exposure to all glassware, equipment, solvents and reagents. An LMB for aqueous sample analyses is prepared by adding a specified volume of surrogate spiking solution to 1-liter of organic-free water (ASTM Type I reagent grade). An LMB for soil/sediment sample analyses is prepared by adding a specified volume of surrogate spiking solution to 10 g of certified organic contaminant-free soil. The volume of surrogate added should be the same as used for samples.

At least seven (7) replicate matrix-specific LMBs should be extracted, fractionated and analyzed, and the mean concentration of Target PAH Analytes and hydrocarbon ranges determined, as appropriate. Data produced (mean Target PAH 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 5-1: 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 RL (lowest Target PAH Analyte calibration or collective hydrocarbon range calibration standard) for either a Target PAH Analyte or hydrocarbon range is considered unacceptable, and indicates that laboratory and/or LMB contamination is present. The source of the non-conformance must be identified and corrected prior to conducting any sample analysis. For purposes of acceptable system background demonstration, concentrations are determined using Equations 6 through 9 in Section 9.9 of the method for Target PAH Analytes and collective hydrocarbon ranges. Calculated concentrations below the lowest calibration standard, including zero (zero area), may be used in these calculations.

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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 concentrations. An LCS must be prepared and treated exactly as a typical field sample submitted for analysis, including fractionation and exposure to all glassware, equipment, solvents and reagents. See Section 10.2.7 of the method for how to prepare the LCS.

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

Equation 5-2: 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 LCS 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 40-140% of the true value.

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 LCS analyses for Target PAH Analytes and hydrocarbon ranges, as indicated below. The %RSD must be ≤25 for both aqueous and soil/sediment samples.

Equation 5-3: 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 analyses.

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5.0 Initial Demonstration of Fractionation Efficiency

A mixed aliphatic and aromatic hydrocarbon fractionation check solution (FCS) is used to evaluate the separation efficiency of the silica gel cartridge/column and to establish the optimum hexane volume to efficiently elute aliphatic hydrocarbons while not allowing significant aromatic hydrocarbon breakthrough. The FCS is prepared as per Section 7.9 of the method.

5.1 To demonstrate the capability of properly fractionating aliphatic and aromatic hydrocarbons, at least four (4) replicate FCSs (see Section 7.9) should be fractionated (using the fractionation procedures detailed in Section 9.2) and analyzed, and the mean measured concentration ($C_{x\ mean}$) of the individual fractionation check compounds determined (see below).

5.2 For each analyte included in the FCS, excluding n-nonane, the mean percent recovery for four (4) replicate samples, expressed as a percentage of the true value, must be between 40% and 140%. Lower recoveries are permissible for n-nonane. If recovery of n-nonane is <30%, the source of the problem should be found and the fractionation check repeated.

Equation 5-4: Calculation of Mean Percent Recovery

$$\text{Mean Percent Recovery} = \frac{C_{x\ mean}\ *}{\text{True Concentration}} \text{ X } 100$$

$$* C_{x\ mean} = \frac{C_1 + C_2 + C_3 \ldots\ldots. C_n}{n}$$

5.3 Subsequent to the IDLC, it is recommended that a FCS be analyzed for each new lot of silica gel/cartridges, to re-establish the optimum volume of hexane elution. **NOTE: Within the same lot of cartridges, different mesh sizes and cartridge weights could exist. It is advisable to evaluate fractionation efficiency on a more frequent basis for large lots (> 500 units) to ensure consistent performance.**

6.0 Method Detection Limit (MDL) Determination

The determination of MDL for the MassDEP EPH Method is optional. The RL for the method is defined as the lowest calibration standard. Determination of the lowest detectable concentration of Target PAH 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 EPH Method do not approach (are considerably higher than) the sensitivity limits of the EPH Method for either Target PAH Analytes or hydrocarbon ranges and are generally more than adequate to meet the most stringent regulatory requirements of the MCP (exception may be for select PAHs compared to GW-1 standards).

An MDL may be established for Target PAH 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 EPH Method.

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

To determine MDL values, take seven (7) replicate aliquots of reagent water fortified at the estimated or "calculated" MDL concentration 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 5-5: 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

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Table 5-1 Initial Demonstration of Laboratory Capability QC Requirements for EPH Analyses

Reference Section	Requirement	Specification & Frequency	Acceptance Criteria
2.0	Initial Demonstration of Acceptable System Background (Optional)	Analyze at least 4 replicate Laboratory Method Blanks (LMB) fortified with surrogate spiking solution. Calculate the mean recovered concentration for each Target PAH analyte and hydrocarbon range. See Equation 5-1 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 seven (7) replicate LCSs fortified with EPH calibration standards at 50% of the highest calibration standard concentration. Calculate the mean recovered concentration $C_{mean.}$ for each Target PAH analyte and hydrocarbon range. See Equation 5-2 in Section 3.0.	The C_{mean} must be 40-140% of the true value of the aliphatic and aromatic hydrocarbon ranges and Target PAH 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 for each Target PAH analyte and hydrocarbon range. See Equation 5-3 in Section 4.0.	The %RSD must be ≤25 for both aqueous and soil/sediment samples.
5.0	Initial Demonstration of Fractionation Efficiency	Fractionate and analyze four (4) replicate FCSs at a concentration of 200 µg/L. A mixed aliphatic and aromatic hydrocarbon FCS is used to evaluate the separation efficiency of the silica gel cartridge/column.	The mean percent recovery for four (4) replicate samples, expressed as a percentage of the true value, must be between 40% and 140%. Lower recoveries (30%) are permissible for n-nonane.
6.0	Method Detection Limit (MDL) Determination (Optional)	Select a fortifying level at the estimated or "calculated" MDL or RL for the LCS. Analyze these 7 replicate low-level LCSs over multiple days and calculate the MDL using Equation 5-5 in Section 6.1. Do not subtract any blank contribution to this value.	See 40 CFR 136, Appendix B The MDL must be < ½ of the RL for individual Target PAH Analytes and < ½ of the RL for collective EPH hydrocarbon ranges.
Continuing QC for each Analytical Batch (up to 20 samples of a similar matrix analyzed contemporaneously)			