WSC – 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)

IV. Petroleum Hydrocarbon Methods

B. Quality Control Requirements and Performance Standards for WSC-CAM-IV B (Extractable Petroleum Hydrocarbons [EPH])

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ACRONYM LIST

CAM	**Compendium of Analytical Methods**
CASN	**Chemical Abstracts Service Number**
CCAL	**Continuing calibration**
%D	**Percent difference or percent drift**
DF	**Dilution factor**
FID	**Flame ionization detector**
GC	**Gas chromatograph**
GC/MS	**Gas chromatography/mass spectrometry**
HCl	**Hydrochloric acid**
ICV	**Initial calibration verification**
IRAs	**Immediate Response Actions**
LCS	**Laboratory control sample**
MassDEP	**Massachusetts Department of Environmental Protection**
MCP	**Massachusetts Contingency Plan**
MD	**Matrix duplicate**
MGP	**Manufactured gas plant**
mL	**milliliter**
MOHML	**Massachusetts Oil and Hazardous Materials List**
MS	**Matrix spike**
MSD	**Matrix spike duplicate**
MTBE	**Methyl tertiary butyl ether**
NA	**Not applicable**
PID	**Photoionization detector**
QA	**Quality assurance**
QC	**Quality control**
r	**Correlation Quality control coefficient**
r^2	**Coefficient of determination**
RAO	**Response Action Outcome**
RCs	**Reportable Concentrations**
RL	**Reporting limit**
RPD	**Relative percent difference**
RQs	**Reportable Quantities**
%R	**Percent recovery**
%RSD	**Percent relative standard deviation**
SIM	**Selective ion monitoring**
TPH	**Total petroleum hydrocarbons**
TSP	**Trisodium phosphate dodechaydrate**
UCM	**Unresolved complex mixture**
µg/kg	**micrograms per kilogram**
µg/L	**micrograms per liter**
VOC	**Volatile organic compound**
VPH	**Volatile petroleum hydrocarbons**

1.0 Quality Control Requirements and Performance Standards for WSC-CAM-IV B

1.1 Overview of WSC-CAM-IV B

WSC-CAM-IV B, *Quality Control Requirements and Performance Standards for the Method for the Determination of Extractable Petroleum Hydrocarbons in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*, is a component of MassDEP's Compendium of Analytical Methods (CAM). Effective July 1, 2010, this revised CAM protocol, WSC-CAM-IV B, *Quality Control Requirements and Performance Standards for the Analysis of Extractable Petroleum Hydrocarbons in Support of Response Actions under the Massachusetts Contingency Plan (MCP)* replaces the original EPH CAM document, WSC-CAM-IV B (effective date, September 10, 2004). Refer to WSC-CAM-I A for an overview of the CAM process. Please note that while this protocol must be followed on and after the effective date of July 1, 2010 for the purpose of "Presumptive Certainty," the revised protocol may be used optionally prior to its effective date upon its publication on April 15, 2010.

This document provides Quality Control (QC) requirements and performance standards to be used in conjunction with the required analytical method MassDEP EPH (May 2004, Revision 1.1), analysis for EPH in aqueous and solid samples by gas chromatography/flame ionization detection (GC/FID) preceded by conventional sample preparation methods via SW-846 Methods, as described in Section 1.3 of this protocol. The QC requirements and performance standards specified in this document in Table IV B-2 together with the analytical procedures described in the MassDEP Method, *Method for the Determination of Extractable Petroleum Hydrocarbons (EPH)*, Revision 1.1 (May 2004) constitute the WSC-CAM-IV B protocol. All protocols included in the CAM are considered "methods" published by the MassDEP pursuant to the provisions of 310 CMR 40.0017(2). Use of the MassDEP EPH method is a "Presumptive Certainty" requirement of WSC-CAM-IV B. Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for EPH analyzed in support of MCP decision-making are presented in Appendix IV B-1 of this document and Appendix VII-A of WSC-CAM-VII A *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)*. Data reporting requirements are also provided in WSC-CAM-VII A.

Overall usability of data produced using this CAM protocol should be evaluated for compliance with project-specific data quality objectives, regardless of "Presumptive Certainty" status. For more guidance on data usability, refer to MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*.

1.1.1 Reporting Limits for WSC-CAM-IV B

The reporting limit (RL) for an individual compound using WSC-CAM-IV B is dependent on the concentration of the lowest non-zero standard in the initial calibration, analyzed under identical conditions as the sample, with adjustments made for the sample size, extraction concentration factor, percent solids, dilution factors, etc., as required. The CAM RLs for WSC-CAM-IV B target analytes and hydrocarbon ranges are:

- 200-500 µg/kg (wet weight) for target polycyclic aromatic hydrocarbons (PAHs) in soil/sediment samples (assuming 100% solids);

- 20,000 µg/kg (wet weight) for each hydrocarbon range in soil/sediment samples (assuming 100% solids);
- 10,000 µg/kg (wet weight) for total petroleum hydrocarbons (TPH) in soil/sediment samples (assuming 100% solids);
- 2-5 µg/L for target PAHs in aqueous samples (surface water, groundwater, and drinking water);
- 100 µg/L for each hydrocarbon range in aqueous samples (surface water, groundwater, and drinking water); and
- 100 µg/L for TPH in aqueous samples (surface water, groundwater, and drinking water).

These values are readily achievable using FIDs. For "Presumptive Certainty" purposes, if the CAM RLs are not achieved, respond "NO" to Question G of the "MassDEP MCP Analytical Protocol Certification Form" and address the CAM RL exceedance in the laboratory narrative.

Reporting limits lower than the above-referenced CAM RLs for WSC-CAM-IV B target analytes may be required to satisfy project requirements. The RL (based on the concentration of the lowest calibration standard) for each contaminant of concern must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 1 Standards, benchmark values, background, etc.). Meeting MCP standards or criteria for target PAHs may require method modifications, such as using gas chromatography/mass spectrometry (GC/MS) with selective ion monitoring (SIM) to improve sensitivity. All such modifications must be described in the laboratory narrative. Regardless of the modification that is used, RLs for the WSC-CAM-IV B target PAHs and hydrocarbon ranges will be proportionately higher for samples that require dilution, when a reduced sample size is used, or for an increased final extract volume.

1.1.2 Initial Demonstration of Proficiency for WSC-CAM-IV B

Each laboratory that uses the WSC-CAM-IV B protocol is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and the analysis of laboratory control samples (LCSs) and LCS duplicates to assess analytical accuracy and precision. Matrix spikes (MS), matrix spike duplicates (MSD) or matrix duplicates may also be used to evaluate accuracy and precision when such samples are analyzed either at the discretion of the laboratory or at the request of the data user.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Table IV B-2 of this protocol. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in the MassDEP EPH method (Section 10.3 and Appendix 5). The data associated with the Initial Demonstration of Proficiency must be kept on file at the laboratory and made available to potential data users on request. The data associated with the Initial Demonstration of Proficiency for WSC-CAM-IV B must include the following information:

QC Element	Performance Criteria
Initial Calibration	WSC-CAM-IV B, Table IV B-2
Continuing Calibration	WSC-CAM-IV B, Table IV B-2

QC Element	Performance Criteria
Method Blanks	WSC-CAM-IV B, Table IV B-2
Average Recovery	MassDEP EPH Method, Appendix 5, Section 3
% Relative Standard Deviation	MassDEP EPH Method, Appendix 5, Section 4
Fractionation Check Standard	MassDEP EPH Method, Appendix 5, Section 5
Surrogate Recovery (extraction and fractionation)	WSC-CAM-IV B, Table IV B-2

NOTE: Because of the number of QC elements associated with the Initial Demonstration of Proficiency, it should be expected that one or more analytes may not meet the performance standard for one or more QC elements. Under these circumstances, the analyst should attempt to locate and correct the problem and repeat the analysis for all non-conforming analytes. All non-conforming analytes along with the laboratory-specific acceptance criteria should be noted in the Initial Demonstration of Proficiency documentation.

It is essential that laboratory-specific performance criteria for LCS, LCS duplicate and surrogate recoveries also be calculated and documented as described in SW-846 Method 8000B, Section 8.7. Experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices; the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent QC performance standards described in Table IV B-2 to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

For the WSC-CAM-IV B protocol, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table IV B-2. It should be noted that the performance standards listed in Table IV B-2 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory.

This protocol is restricted to use by, or under the supervision of, analysts experienced in the use of GC instrumentation as a quantitative tool and skilled in the interpretation of chromatograms for individual target PAHs and petroleum hydrocarbon ranges.

1.2 Summary of MassDEP EPH Method

A sample submitted for EPH analysis is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated in a Kuderna-Danish apparatus. Sample cleanup and separation into aliphatic and aromatic fractions is conducted using commercially available silica gel cartridges or self-packed silica gel columns. The two extracts produced (i.e., an aliphatic extract and an aromatic extract) are then re-concentrated to final volumes of 1 mL each. The extracts are then separately analyzed by a capillary column gas chromatograph equipped with a flame ionization detector. The resultant chromatogram of aliphatic compounds is collectively integrated within the C_9 through C_{18} and C_{19} through C_{36} ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C_{11} through C_{22} range, and is (optionally) used to identify and quantify individual concentrations of Diesel and/or other Target PAH Analytes. It should be noted that the

chromatogram resulting from the analysis of an extract which has not been fractionated is collectively integrated within the C_9 through C_{36} range to provide the concentration of TPH.

Average calibration factors (or calibration curves) determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of C_9 through C_{18} and C_{19} through C_{36} aliphatic hydrocarbons. An average calibration factor (or calibration curve) determined using a PAH standard mixture is used to calculate a collective concentration of C_{11} through C_{22} aromatic hydrocarbons. Calibration factors (or calibration curves) determined for individual components of the PAH standard mixture are also used to calculate individual concentrations of Diesel and Target PAH Analytes. The EPH Method marker compounds and retention time windows are summarized in Table IV B-1.

Table IV B-1: EPH Method Range Marker Compounds

Hydrocarbon Range	Beginning Marker Compound	Ending Marker Compound
C_9-C_{18} Aliphatic Hydrocarbons	0.1 minutes before n-nonane	0.1 minutes before n-nonadecane
C_{19}-C_{36} Aliphatic Hydrocarbons	0.1 minutes before n-nonadecane	0.1 minutes after n-hexatriacontane
C_{11}-C_{22} Aromatic Hydrocarbons	0.1 minutes before naphthalene	0.1 minutes after benzo(g,h,i)perylene

The samples are prepared for GC analysis using the appropriate sample preparation (See Section 1.3) procedure followed by fractionation.

After fractionation, the extract is analyzed by injecting a 1 to 2-µL aliquot into a gas chromatograph with a narrow- or wide-bore fused silica capillary column. The GC oven is temperature-programmed to facilitate separation of the analytes of interest, which are then detected by an FID that is interfaced directly to the gas chromatograph.

Identification of target PAHs analytes is accomplished by comparing the sample retention time with the retention time of standards obtained under identical analytical conditions. Quantitation is accomplished by using the peak area and a calibration factor (or calibration curve) generated from a minimum five-point calibration curve.

1.3 Sample Extraction/Cleanup Methods for WSC-CAM-IV B

Samples for analysis by the MassDEP EPH Method must be extracted or diluted using one of the following methods.

SW-846 Extraction 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)

SW-846 Extraction Method	Matrix	Description
3546	Soil/Sediment	Microwave Extraction
3570	Soil/Sediment	Microscale Solvent Extraction (MSE)
3550C	Contaminated Solids[1]	Ultrasonic Extraction
3580A	NAPL	Waste Dilution

[1]**Sonication may only be used for the extraction of highly contaminated (free product) non-soil/sediments (debris). Any other use of ultrasonic extraction is not allowed.**

After solvent exchange with hexane, the extract is concentrated and subjected to a silica gel cleanup and fractionation step to isolate the aromatic and aliphatic components of the sample prior to GC analysis. It should be noted that the recommended hexane elution volume (20 mL) is critical and may need to be adjusted for each lot of silica gel/cartridges to optimize sample extraction and fractionation efficiencies. See Section 10.4.3.7 and Appendix 5 of the EPH Method for specifications on the use and evaluation of Fractionation Check Solutions.

1.4 Method Interferences

- Refer to SW-846 Methods 3500C (Section 4.0, in particular), 3600C, and 8000B for a detailed discussion of interferences associated with the preparatory and GC methods. Analytical interferences and interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are referenced or provided as part of the EPH method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into four broad categories.

  - Contaminated solvents, reagents, or sample processing hardware,
  - Contaminated GC carrier gas, parts, column surfaces, or detector surfaces,
  - Non-target compounds simultaneously extracted from the sample matrix which cause a detector response, and
  - Co-elution of target analytes.

  An in depth discussion of the causes and corrective actions for all of these interferences is beyond the scope of this guidance document. A brief discussion of the more prevalent interferences is presented below.

- The major contaminant source for the EPH Method is attributable to the leaching of plasticizers or other contaminants from silica gel SPE cartridges. Preferably, the silica gel cleanup and fractionation procedure described in Section 9.2 of the EPH Method should be used to minimize this source of interference.

  As described in Section 11.2.6 of the EPH Method, peaks identified during the injection of Laboratory Method Blanks, and determined to be attributable to the previously described silica gel SPE cartridge interference, may adversely affect the accurate integration of the C_{11}-C_{22} aromatic hydrocarbon range area. In general, blank correction, either by the manual or automatic subtraction of contaminant peaks, **is not permissible** unless the laboratory performs a GC/MS analysis of the Laboratory Method Blank extract to confirm that the encountered contaminant(s) is not a C_{11}-C_{22} aromatic

hydrocarbon range compound. The laboratory must provide a discussion in the laboratory narrative if this approach is used.

- Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of semivolatile organics. After the analysis of a sample containing high concentrations of semivolatile organics, one or more blanks should be analyzed to check for potential cross-contamination/carryover. Concentrations of target PAHs or hydrocarbon ranges which exceed the upper limit of calibration should prompt the analyst to check for potential cross-contamination/carryover. In addition, samples containing large amounts of water-soluble materials, suspended solids, or high boiling point compounds may also present potential for cross-contamination/carryover. Laboratories should be aware that carryover from high boiling point compounds may not appear until a later sample analysis. To reduce carryover, the sample syringe must be rinsed with solvent between sample injections.

1.5 Quality Control Requirements for WSC-CAM-IV B

1.5.1 General QC Requirements

Refer to SW-846 Method 8000B for general QC procedures for all chromatographic methods. Instrument QC and method performance requirements for the GC/FID system may be found in Section 10 of the MassDEP EPH Method.

1.5.2 Specific QC Requirements and Performance Standards for WSC-CAM-IV B

Specific QC requirements and performance standards for the WSC-CAM-IV B protocol are presented in Table IV B-2. Refer to WSC-CAM-VII A for field QC requirements. Strict compliance with the QC requirements and performance standards, as well as satisfying the CAM's other analytical and reporting requirements will provide a data user with "Presumptive Certainty" in support of Response Actions under the MCP. The concept of "Presumptive Certainty" is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" of data acceptance by agency reviewers. In order to achieve "Presumptive Certainty" for analytical data, parties must:

(a) Use the analytical method specified for the selected CAM protocol;
(b) Incorporate **all** required analytical QC elements specified for the selected CAM protocol;
(c) Implement, as necessary, required corrective actions and analytical response actions for **all** non-conforming analytical performance standards;
(d) Evaluate and narrate, as necessary, **all** identified CAM protocol non-compliances; and
(e) Comply with **all** the reporting requirements specified in WSC-CAM-VII A, including retention of reported and unreported analytical data and information for a period of ten (10) years.

In achieving "Presumptive Certainty" status, parties will be assured that analytical data sets:

- ✓ Satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data; and

- ✓ May be used in a data usability and representativeness assessment, as required in 310 CMR 40.1056(2)(k) for Response Action Outcome (RAO) submittals, consistent with the guidance described in MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*.

1.6 Special Analytical Considerations for WSC-CAM-IV B

The following bullets highlight potential issues that may be encountered with the analysis of EPH using this protocol.

- 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 petroleum-based lubricating oils. The EPH Method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, or other petroleum products, that contain lower or higher boiling components or distillates of aliphatic and/or aromatic hydrocarbons that are outside the hydrocarbon ranges (C_9 through C_{36} aliphatic and C_{11} through C_{22} aromatic ranges) of the MassDEP EPH Method.

- Both EPH target PAH analytes and hydrocarbon ranges are subject to potential "false positive" bias associated with non-specific gas chromatographic analysis. Confirmatory analysis by a GC/MS procedure 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 hydrocarbon compound not meeting the regulatory definition of a specific hydrocarbon fraction is suspected.

  - ➢ Other compounds co-eluting at the specified retention time may be incorrectly identified and/or quantified (false positive) as a target PAH analyte; or

  - ➢ Compounds not meeting the regulatory definition of the aromatic and/or aliphatic fractions as defined by this method in Sections 3.4, 3.5 and 3.6 of the EPH Method that elute within the method-defined retention time window would be included in the total area and thus, the result, and would therefore be an overestimation of the hydrocarbon range's concentration. If the concentration of a hydrocarbon range is based on one (or just a few) peaks within the range and an indicative petroleum hydrocarbon peak pattern is not apparent, the laboratory should provide this information and alert the data user of the potential for a false positive result in the laboratory narrative. MCP sites with co-mingled non-petroleum hydrocarbons such as vegetable oils, synthetic oils and lubricants, and some naturally occurring humic materials are particularly susceptible to this type of interference.

- Potential biases may occur due to inefficient fractionation procedures.

  - ➢ The lighter aromatic compounds may be stripped or may break through the silica gel cartridge/column because of mass overloading resulting in an underestimation of the C_{11}-C_{22} aromatic hydrocarbon concentration.

  - ➢ The amount of hexane used to elute the aliphatic component of the EPH hydrocarbon mixture is critical. An excessive volume of hexane may cause the lighter aromatics to breakthrough and be captured in the aliphatic fraction while an insufficient volume of hexane may allow some of the heavier aliphatic hydrocarbons to be retained on the silica gel cartridge/column resulting in a lower recovery for these

aliphatic fractions. Depending on the analytical conditions, this could result in an underestimation of the C_{11} through C_{22} aromatic range concentration for the excessive hexane condition or an overestimation of the aromatic range concentration for the deficient hexane condition. It should be noted that acceptable recovery of the Fractionation Surrogate Standards, described in Section 7.5 of the EPH Method, may not always provide absolute confirmation that effective separation of the aliphatic fraction from the aromatic fraction of the sample extract has been accomplished.

- If ineffective fraction separation is suspected, even with acceptable recovery of the Fractionation Surrogate Standards, SW-846 Method 8270D, WSC-CAM-II B, Semivolatile Organics by GC/MS, may be employed to accurately identify and quantify the components that comprise a suspect fraction to resolve the uncertainty. Alternatively, if aromatic breakthrough is suspected, the aliphatic fraction may be analyzed to determine if naphthalene or any of the other more "mobile" aromatics are present. See Section 10.4.2 of the EPH Method.

- If ineffective fraction separation is confirmed, the elution volume for optimal fractionation efficiency for the specific silica gel lot should be re-established as described in Section 10.4.3.7 of the EPH Method. ***For particularly difficult separations, it may be required to resort to multiple cartridge or column cleanup/fractionation.***

- TPH is defined as the collective concentration associated with the total area count for all peaks corresponding to any fractionated or unfractionated aliphatic and/or aromatic compounds eluting between 0.1 minutes before the retention time for n-C_9 to 0.1 minutes after the Rt for n-C_{36}, **excluding** the area counts of the individual target PAH Analytes, surrogates, and/or internal standards that co-elute within this chromatographic range. MassDEP recommends that the analysis of the unfractionated EPH extract be used as a conservative estimate of TPH, as this term is defined in 310 CMR 40.0006, when this parameter is used to support human health risk characterization or other MCP assessments and evaluation decisions.

- In general, it may be prudent to confirm all FID data using SW-846 Method 8270D (GC/MS) if critical MCP decision-making (notification, compliance with cleanup standards, risk assessment, etc.) is based solely on the EPH Method (or any other non-specific GC analysis). If a positive interference is suspected from hydrocarbons and/or non-hydrocarbons not associated with EPH in either aliphatic or the aromatic fraction or with a target PAH analyte, and such interference would adversely affect MCP decision-making, if confirmed, then SW-846 Method 8270D, WSC-CAM-II B, Semivolatile Organics by GC/MS, should be employed to accurately identify and quantify the components that comprise a hydrocarbon range or to resolve any uncertainty regarding these identifications.

  It is recommended that the chromatographic conditions specified under SW-846 Method 8270D be modified for consistency with the conditions specified by the EPH Method to better allow for a direct comparison of the suspect FID peaks with the GC/MS system. This is particularly useful when comparing "suspect" aliphatic hydrocarbons. The electron impact mass spectra for aliphatic hydrocarbon homologues are not particularly unique and chromatographic relative retention time data may also be required to confirm suspect EPH data.

- 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 of the EPH Method are satisfied.

- The EPH Method discusses "significant modifications", such as the use of a GC/MS detector to identify and quantify the EPH aliphatic and aromatic hydrocarbon ranges of an **un-fractionated** sample extract, provided that adequate documentation exists, or has been developed to demonstrate an equivalent or superior level of performance. Be advised, however, that any adaptation to the EPH Method that constitutes a "significant modification" pursuant to Section 11.3.1.1 will preclude obtaining "Presumptive Certainty" status for any analytical data produced using such modification and must be disclosed and documented on an attachment to the EPH Method analytical report form, as described in Section 11.3 and Appendix 3 of the EPH Method.

- A linear or non-linear calibration model must not be used to compensate for detector saturation or to avoid proper instrument maintenance. As such, linear or non-linear regression must not be employed for initial calibration calculations that typically meet percent relative standard deviation (%RSD) requirements specified in Table IV B-2.

Table IV B-2: Specific QC Requirements and Performance Standards for Extractable Petroleum Hydrocarbons (EPH) Using WSC-CAM-IV B[1]

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[2]	Required Corrective Action	Required Analytical Response Action
Initial Demonstration of Proficiency	Laboratory Analytical Accuracy & Precision	(1) Must be performed prior to using method on samples. (2) Must be performed for each matrix. (3) Must contain all target analytes. (4) Must follow procedure in Appendix 5 of the EPH method.	No	NA	Refer to Appendix 5 of the EPH method and Section 1.1.2 of this protocol.	NA
GC Performance	Inter-laboratory Consistency and Comparability	(1) PAH resolution as per Section 10.1.3 of the EPH method. (2) C_9 resolution from solvent front. (3) Response ratio of C_{28} to C_{20} must be $\geq$0.85. (4) Surrogates and internal standards must be resolved from all aromatic and aliphatic standards. (5) Naphthalene and n-dodecane in the aliphatic fraction must be adequately resolved (see Section 10.4.2 of the EPH Method).	No	NA	Perform instrument/injection port maintenance as necessary.	Suspend all subsequent analyses until performance criteria are achieved. Report exceedances in the laboratory narrative.
Retention Time Windows	Laboratory Analytical Accuracy	(1) Prior to initial calibration and when a new GC column is installed. (2) Calculated according to the method (Section 9.6). (3) Retention time windows must be updated with every CCAL.	No	NA	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) Must be analyzed at least once prior to analyzing samples, when initial calibration verification or continuing calibration does not meet the performance standards, and when major instrument maintenance is performed. (2) Minimum of 5 standards (or 6 if non-linear regression used). (3) Low standard must be $\leq$RL. (4) %RSD $\leq$25, r $\geq$0.99 (linear regression), or r^2 $\geq$0.99 (non-linear regression) for each target compound and hydrocarbon range.	No	NA	(1) Recalibrate as required by method. (2) If recalculated concentrations from the lowest calibration standard are outside of 70-130% recovery range, either: * The RL must be reported as an estimated value[3], or * The RL must be raised to the concentration of the next highest calibration standard	Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds (%RSD >25, r <0.99, or r^2 <0.99) in laboratory narrative. If non-linear regression (i.e., quadratic equation) is used for calibration, this must be noted in the laboratory narrative along with the compounds affected.

Table IV B-2: Specific QC Requirements and Performance Standards for Extractable Petroleum Hydrocarbons (EPH) Using WSC-CAM-IV B[1]

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[2]	Required Corrective Action	Required Analytical Response Action
		(5) If %RSD >25, linear or non-linear regression must be used. (6) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. (7) Must meet GC performance standards described in Section 10.2 of the EPH method. (8) Calibration must be performed under the same conditions as the samples. (9) If linear or non-linear regression used, verify the RL by recalculating concentrations in lowest calibration standard using the final calibration curve; recoveries must be 70-130%.			that exhibits acceptable recoveries when recalculated using the final calibration curve.	
Initial Calibration Verification	Laboratory Analytical Accuracy	(1) Immediately after each initial calibration. (2) Concentration level near midpoint of curve. (3) Prepared using standard source different than used for initial calibration. (4) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. (5) Percent recoveries must be between 80-120% for each target analyte.	No	NA	Locate source of problem; recalibrate if >10% of all analytes are outside of criteria.	If recovery is outside of 80-120% for any analyte, report non-conforming compounds in laboratory narrative.
Continuing Calibration	Laboratory Analytical Accuracy	(1) Prior to samples, every 24 hours or every 20 samples, whichever is more frequent, and at the end of the analytical sequence. (2) Concentration level near midpoint of curve. (3) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables	No	NA	(1) Perform instrument maintenance, reanalyze continuing calibration and/or recalibrate as required by method. (2) Renalyze "associated samples" if beginning or ending continuing calibration exhibited low	Report non-conforming compounds (%D >25) and associated samples in laboratory narrative.

Table IV B-2: Specific QC Requirements and Performance Standards for Extractable Petroleum Hydrocarbons (EPH) Using WSC-CAM-IV B[1]

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[2]	Required Corrective Action	Required Analytical Response Action
		1 and 2 of the EPH method. (4) Opening CCAL: %D or % drift must be ≤25 for all target PAH analytes and ranges except for n-nonane, which must be ≤30. (5) Closing CCAL: Up to four (4) compounds may exhibit a %D or % drift >25 but <40. (6) Must meet GC performance standards. (7) Verify that all analytes fall within retention time windows.			response. (3) Reanalyze "associated samples" if beginning or ending continuing calibration exhibited high response and associated EPH target PAHs and hydrocarbon ranges were detected in the "associated samples." NOTE: "Associated samples" refers to all samples analyzed since the last acceptable continuing calibration.	
Method Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Matrix-specific (e.g., water, soil). (3) EPH hydrocarbon ranges must be ≤10% of the most stringent applicable MCP standard for solid samples and ≤50% of the most stringent applicable MCP standard for aqueous samples. (4) Target PAH analytes must be <RL.	Yes	NA	(1) If concentration of contaminant in sample is <10x concentration in blank, locate source of contamination; correct problem; re-extract and re-analyze method blank and associated samples. (2) No corrective action required if concentration of contaminant in sample is >10x concentration in blank or if contaminant not detected in sample.	(1) If sample re-extraction is not possible, report non-conformance in laboratory narrative. (2) If contamination of method blanks is suspected or present, the laboratory, using a "B" or some other convention, should qualify the sample results. Blank contamination should also be documented in the laboratory narrative. (3) If re-extraction is performed within holding time and yields acceptable method blank results, the laboratory

Table IV B-2: Specific QC Requirements and Performance Standards for Extractable Petroleum Hydrocarbons (EPH) Using WSC-CAM-IV B[1]

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[2]	Required Corrective Action	Required Analytical Response Action
						may report results of the re-extraction only. (4) If re-extraction is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction.
Laboratory Control Sample (LCS)	Laboratory Analytical Accuracy	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Prepared using standard source different than used for initial calibration. (3) Concentration level near midpoint of curve. (4) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH method. (5) Matrix-specific (e.g., soil, water). (6) Percent recoveries must be between 40-140% for target analytes and hydrocarbon ranges*, except for nonane which must be between 30-140%. (7) The individual concentrations of both naphthalene and 2-methylnaphthalene must be <5% in aliphatic fraction. (See calculation in the EPH Method, Section 10.4.2.) (8) Must be prepared in a water-miscible solvent (e.g., acetone, methanol). *Percent recoveries for the individual compounds used for the calibration of the aliphatic and aromatic ranges must be evaluated.	Yes	Recovery <10%; affects nondetect results for affected analyte in all samples extracted with this LCS.	(1) Locate source of problem; re-extract and re-analyze LCS and associated samples if >10% of all analytes are outside of criteria. (2) If ≤10% of compounds are outside of the acceptance criteria, re-extraction is not required as long as recoveries are >10%. (3) If >10% of compounds are above the acceptance criteria (>140%), reextraction is not required if affected compounds were not detected in associated samples. (4) Re-fractionate archived batch extracts if either the concentration of naphthalene and/or 2-methylnaphthalene in aliphatic fraction is >5% of either of their respective total concentrations.	(1) If sample re-extraction is not possible, report non-conformance in laboratory narrative. (2) If recovery is outside of 40-140% for any analyte, report non-conforming compounds in laboratory narrative. (3) If re-extraction or re-fractionation is performed within holding time and yields acceptable LCS results, the laboratory may report results of the re-extraction or re-fractionation only. (4) If re-extraction or re-fractionation is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction or re-fractionation.

Table IV B-2: Specific QC Requirements and Performance Standards for Extractable Petroleum Hydrocarbons (EPH) Using WSC-CAM-IV B[1]

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[2]	Required Corrective Action	Required Analytical Response Action
LCS Duplicate	Laboratory Analytical Accuracy & Precision	(1) Extracted with every batch or every 20 samples, whichever is more frequent. (2) Prepared using standard source different than used for initial calibration. (3) Concentration level near midpoint of curve. (4) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH method. (5) Matrix-specific (e.g., soil, water). (6) Percent recoveries must be between 40-140% for target analytes and hydrocarbon ranges*, except for nonane which must be between 30-140%. (7) The individual concentrations of both naphthalene and 2-methylnaphthalene must be <5% in aliphatic fraction. (See calculation in the EPH Method, Section 10.4.2.) (8) RPDs must be ≤25 for waters and solids. (9) Must be prepared in a water-miscible solvent (e.g., acetone, methanol). *Percent recoveries for the individual compounds used for the calibration of the aliphatic and aromatic ranges must be evaluated.	Yes	Recovery <10%; affects nondetect results for affected analyte in all samples extracted with this LCS.	(1) Locate source of problem; re-extract and re-analyze LCS and associated samples if >10% of all analytes are outside of recovery acceptance criteria. (2) If ≤10% of compounds are outside of the recovery acceptance criteria, re-extraction is not required as long as recoveries are >10%. (3) If >10% of compounds are above the recovery acceptance criteria (>140%), reextraction is not required if affected compounds were not detected in associated samples. (4) Re-fractionate archived batch extracts if either the concentration of naphthalene and/or 2-methylnaphthalene in aliphatic fraction is >5% of either of their respective total concentrations.	(1) If sample re-extraction is not possible, report non-conformance in laboratory narrative. (2) If recovery is outside of 40-140% or RPD >25 for any analyte, report non-conforming compounds in laboratory narrative. 3) If re-extraction or re-fractionation is performed within holding time and yields acceptable LCS results, the laboratory may report results of the re-extraction or re-fractionation only. (4) If re-extraction or re-fractionation is performed outside of holding time, the laboratory must report results of both the initial extraction and re-extraction or re-fractionation.
MS/MSD	Method Accuracy & Precision in Sample Matrix	(1) Every 20 samples (at discretion of laboratory or at request of data user). (2) Prepared using standard source different than used for initial calibration. (3) Concentration level near midpoint of curve.	Yes ONLY when requested by the data user	Recovery <10%; affects nondetect result for affected analyte in unspiked sample only.	Check LCS; if recoveries are acceptable in LCS, narrate non-conformance.	Note exceedances in laboratory narrative.

Table IV B-2: Specific QC Requirements and Performance Standards for Extractable Petroleum Hydrocarbons (EPH) Using WSC-CAM-IV B[1]

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[2]	Required Corrective Action	Required Analytical Response Action
		(4) Must contain all aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH method. (5) Matrix-specific (e.g., soil, water). (6) Percent recoveries must be between 40-140% for target analytes and hydrocarbon ranges, except for nonane which must be between 30-140%. (7) RPDs ≤50 for waters and solids. (8) Must be prepared in a water-miscible solvent (e.g., acetone, methanol).				
Matrix Duplicates	Method Precision in Sample Matrix	(1) Every 20 samples (at discretion of laboratory or at request of data user). (2) Matrix-specific (e.g., soil, water). (3) RPDs ≤50 for waters and solids for results >5x the reporting limit.	Yes ONLY when requested by the data user	NA	Narrate non-conformance.	Note exceedances (RPDs >50) in laboratory narrative.
Surrogates	Method Accuracy in Sample Matrix	(1) Minimum of 2 extraction surrogates and 1 fractionation surrogate. Recommended extraction surrogates: COD and OTP Recommended fractionation surrogates: 2-bromonaphthalene and 2-fluorobiphenyl (optional) (2) Percent recoveries must be between 40-140% for all surrogates.	Yes	Recovery <10%; affects all associated nondetect results in affected sample. NOTE: OTP non-conformances affect the aromatic extract; COD non-conformances affect the aliphatic extract.	If one or more surrogates are outside of limits or if any one surrogate recovers at <10%: (1) Re-extract the sample or re-fractionate the appropriate extract if surrogate recoveries are low. (2) Re-extract the sample or re-fractionate the appropriate extract if surrogate recoveries are high and associated aliphatic or aromatic analytes were detected in the sample. Re-extraction is not required if one of the	(1) Report recoveries outside of 40-140% in laboratory narrative. (2) If re-extraction yields similar surrogate non-conformances, the laboratory must report results of both the initial extraction and re-extraction. (3) If re-extraction or re-fractionation is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the re-extraction or re-

Table IV B-2: Specific QC Requirements and Performance Standards for Extractable Petroleum Hydrocarbons (EPH) Using WSC-CAM-IV B[1]

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[2]	Required Corrective Action	Required Analytical Response Action
					following exceptions applies: (a) If surrogate recoveries are high and associated target analytes are not detected in sample, re-extraction and/or re-fractionation is not required. (b) Re-extraction and/or re-fractionation is not required if obvious interference present (e.g., UCM). If obvious interference is present and surrogate recovery would cause rejection of data (i.e., <10%), re-analyze sample on dilution. (c) If a surrogate is diluted to a concentration below that of the lowest calibration standard, reextraction and/or reanalysis is not required. NOTE: If re-fractionation is performed and surrogate recoveries do not improve, re-extraction must be performed. NOTE: OTP non-conformances affect the aromatic extract; COD non-conformances affect the aliphatic extract.	fractionation only. (4) If re-extraction or re-fractionation is performed outside of the holding time and yields acceptable surrogate recoveries, the laboratory must report results of both the initial extraction/fractionation and re-extraction/re-fractionation. (5) If sample is not re-extracted or re-fractionated due to obvious interference, the laboratory must provide the chromatogram in the data report.

Table IV B-2: Specific QC Requirements and Performance Standards for Extractable Petroleum Hydrocarbons (EPH) Using WSC-CAM-IV B[1]

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[2]	Required Corrective Action	Required Analytical Response Action
Internal Standards (when GC/MS used for quantification of PAHs and aliphatic/aromatic hydrocarbon ranges after fractionation)	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	(1) Minimum of 1. Recommended internal standard is 5-alpha androstane. Alternatively, COD may also be as an internal standard for GC/MS analysis. (2) Area counts in samples must be between 50 – 200% of the area counts in the associated continuing calibration standard. (3) Retention times of internal standards must be within ±30 seconds of retention times in associated continuing calibration standard.	No	Recovery <20%; affects all nondetect results quantitated using affected internal standard in associated sample.	If internal standard is outside of limits, reanalyze sample unless obvious interference present (e.g., UCM). NOTE: If obvious interference is present and internal standard area would cause rejection of data (i.e., <20%), reanalyze sample on dilution.	(1) Report nonconformances in laboratory narrative. Include actual recovery of internal standard and provide summary of analytes quantitated using the internal standard. (2) If reanalysis yields similar internal standard non-conformances, the laboratory must report results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable internal standard recoveries, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of the holding time and yields acceptable internal standard recoveries, the laboratory must report results of both analyses. (5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.

Table IV B-2: Specific QC Requirements and Performance Standards for Extractable Petroleum Hydrocarbons (EPH) Using WSC-CAM-IV B[1]

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[2]	Required Corrective Action	Required Analytical Response Action
Fractionation Check Standard	Laboratory Method Accuracy	(1) Performed for each new lot of silica gel cartridges. (2) Must contain all EPH aliphatic and aromatic hydrocarbon standards listed in Tables 1 and 2 of the EPH Method. (3) Laboratory–determined percent recoveries must be between 40 -140% for EPH hydrocarbon ranges and target PAH analytes except for n-nonane, which must be between 30-140%. .	No	Recovery <10%; affects nondetect results for affected analyte in all samples fractionated using the associated lot of silica gel cartridges.	Re-fractionate using different volumes of hexane until recoveries are acceptable.	Report recoveries outside of 40-140% in laboratory narrative.
Identification and Quantitation	NA	(1) The laboratory must use the average calibration factor, response factor, linear or non-linear regression curve generated from the associated initial calibration for quantitation of each target analyte and hydrocarbon range. (2) Results must be reported with 2 or more "significant figures" if $\geq$ RL. If reporting values below the RL, report with 1 or more "significant figures".[4]	NA	NA	NA	NA

Table IV B-2: Specific QC Requirements and Performance Standards for Extractable Petroleum Hydrocarbons (EPH) Using WSC-CAM-IV B[1]

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[2]	Required Corrective Action	Required Analytical Response Action
General Reporting Issues	NA	(1) The laboratory must only report values ≥ the sample-specific reporting limit. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported. (3) All information required in Appendix 3 of the EPH Method must be provided for each sample in a "clear and concise manner." (4) Results for soils/sediments must be reported on a dry-weight basis for comparison to MCP regulatory standards. (5) Refer to Appendix IV B-1 for chain-of-custody requirements regarding preservation, cooler temperature, and holding times.	NA	NA	NA	(1) Complete analytical documentation for diluted and undiluted analyses must be made available for review during an audit. (2) The performance of dilutions must be documented in the laboratory narrative or on the report form. Unless due to elevated concentrations of target compounds, reasons for dilutions must be explained in the laboratory narrative. (3) If samples are not properly preserved (pH >2 for aqueous samples) or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory narrative. (4) If samples are extracted and/or analyzed outside of the holding time, note the non-conformances in the laboratory narrative.

[1]If GC/MS is used for the analysis of PAHs and/or hydrocarbon ranges after fractionation, the performance criteria in Table II B-1 of WSC-CAM IIB must be met for the PAHs and the performance criteria in Table IV B-2 above must be met for the hydrocarbon ranges.

[2]As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, September 2007, if these results are observed, data users should consider nondetect results as unusable and positive results as estimated with a significant low bias.

[3]If the RL is estimated due to unacceptable recovery of the lowest standard, the CAM RL has not been achieved; Question G of the "MassDEP MCP Analytical Protocol Certification Form" must be answered "NO" and this must be addressed in the laboratory narrative.

[4]Reporting protocol for "significant figures" is a policy decision included for standardization and consistency for reporting of results and is not a definition of "significant" in the scientific or mathematical sense.

1.7 Analyte List for WSC-CAM-IV B

The MCP analyte list for WSC-CAM-IV B is presented in Table IV B-3. The list is comprised of 17 PAHs, four (4) of which are required for the evaluation of diesel fuel releases, and three (3) collectively quantified extractable hydrocarbon ranges. Use of the EPH Method to identify and quantify the listed target PAH analytes is optional at the discretion of the data user.

It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL for the target analytes. Sources of various MassDEP standards and criteria are as follows:

- Reportable Quantities (RQs) and Concentrations (RCs) as described in 310 CMR 40.1600, The Massachusetts Oil and Hazardous Materials List (MOHML), in Subpart P of the MCP may be found at the following URL: https://www.mass.gov/site-cleanup-regulations-policies-forms-more.
- An online searchable Oil & Hazardous Materials List of RQs and RCs values may be found at the following URL: https://www.mass.gov/service-details/oil-hazardous-material-list.
- An updated list of MCP Method 1 Standards may be found at the following URL: https://www.mass.gov/site-cleanup-regulations-policies-forms-more.

All of the target PAH analytes and hydrocarbon ranges that comprise the MCP Analyte List for the EPH Method have a promulgated MCP Method 1 groundwater/soil standard.

1.7.1 Analyte List Reporting Requirements for WSC-CAM-IV B

While it is not necessary to request and report all the WSC-CAM-IV B analytes listed in Table IV B-3 to obtain "Presumptive Certainty" status, it is necessary to document use and reporting of a reduced analyte list, for site characterization and data representativeness considerations. MassDEP strongly recommends use of the full analyte list during the initial stages of site investigations, and/or at sites with an unknown or complicated history of uses of oil or hazardous materials. These assessment activities may include but are not limited to:

- ✓ Immediate Response Actions (IRAs) performed in accordance with 310 CMR 40.0410;
- ✓ Initial Site Investigation Activities performed in accordance with 310 CMR 40.0405(1);
- ✓ Phase I Initial Site Investigation Activities performed in accordance with 310 CMR 40.0480 through 40.0483; and
- ✓ Phase II Comprehensive Site Investigation Activities performed in accordance with 310 CMR 40.0830

In a limited number of cases, the use of the full analyte list for a chosen analytical method may not be necessary, with respect to data representativeness concerns, including:

- ✓ Sites where substantial site/use history information is available to rule-out all but a limited number of contaminants of concern, and where use of the full analyte list would significantly increase investigative costs; or

- ✓ Well-characterized sites where initial full-analyte list testing efforts have sufficiently narrowed the list of contaminants of concern.

Note: a data user who avoids the detection and quantitation of a contaminant that is present or likely present at a site above background levels by limiting an analyte list could be found in criminal violation of MGL c. 21E or any regulations or orders adopted or issued thereunder.

In cases where a reduced list of analytes is requested, laboratories must still employ the specified QC requirements and performance standards in WSC-CAM-IV B to obtain "Presumptive Certainty" status.

For the EPH Method, 17 PAHs are defined as "Target PAH Analytes". Included in this comprehensive list is a subset of 4 "Diesel PAHs" (naphthalene, 2-methylnaphthalene, phenanthrene, and acenaphthene). For most sites that are known to be contaminated by a release of diesel and/or #2 fuel oil only, Diesel PAHs will be the only target PAHs of interest. For purposes of CAM compliance, if only the Diesel PAHs are requested and reported, this must still be noted in the laboratory narrative.

Table IV B-3: Analyte List for WSC-CAM-IV B (MassDEP EPH)

Analyte	CASN
Extractable Petroleum Hydrocarbon Ranges:	
C_9-C_{18} Aliphatic Hydrocarbons	NA
C_{19}-C_{36} Aliphatic Hydrocarbons	NA
C_{11}-C_{22} Aromatic Hydrocarbons	NA
Diesel PAH Analytes:	
Naphthalene	91-20-3
2-Methylnaphthalene	91-57-6
Phenanthrene	85-01-8
Acenaphthene	83-32-9
Other Target PAH Analytes:	
Fluorene	86-73-7
Acenaphthylene	208-96-8
Anthracene	120-12-7
Fluoranthene	206-44-0
Pyrene	129-00-0
Benzo(a)Anthracene	56-55-3
Chrysene	218-01-9
Benzo(b)Fluoranthene	205-99-2
Benzo(k)Fluoranthene	207-08-9
Benzo(a)Pyrene	50-32-8
Indeno(1,2,3-cd)Pyrene	193-39-5
Dibenzo(a,h)Anthracene	53-70-3
Benzo(g,h,i)Perylene	191-24-2

CASN – Chemical Abstracts Service Numbers
NA – Not Applicable

2.0 Data Usability Assessment

Specific guidance applicable to all Class A, B or C RAO Statements, including partial RAOs, for preparation of Representativeness Evaluations and Data Usability Assessments pursuant to 310 CMR 40.1056(2)(k) of the MCP is provided in *MCP Representativeness Evaluations and Data Usability Assessments* (Policy #WSC-07-350). This document provides general information regarding the purpose and content of these required evaluations as a component of and in support of an RAO submittal. The most current version of this document may be found at the following URL: https://www.mass.gov/site-cleanup-regulations-policies-forms-more.

Overall usability of data produced using this CAM protocol should be evaluated for compliance with project-specific data objectives using MassDEP Policy #WSC-07-350, regardless of "Presumptive Certainty" status.

3.0 Reporting Requirements for WSC-CAM-IV B

3.1 General Reporting Requirements for WSC-CAM-IV B

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM-VII A, Section 2.4. This guidance document provides limited recommendations for field QC, as well as the required content of the laboratory report, which includes:

- Laboratory identification information,
- Analytical results and supporting information,
- Sample- and batch-specific QC information,
- Laboratory Report Certification Statement,
- Copy of the Analytical Protocol Certification Form,
- Laboratory narrative contents, and
- Chain-of-custody form requirements.

3.2 Specific Reporting Requirements for WSC-CAM-IV B

Specific QC requirements and performance standards for WSC-CAM-IV B are presented in Table IV B-2. Specific reporting requirements for WSC-CAM-IV B are summarized below in Table IV B-4 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements must always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data must be available for review during an audit and may also be requested on a client-specific basis.

Soil and sediment results must be reported on a dry-weight basis. Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.

Table IV B-4 Routine Reporting Requirements for WSC-CAM-IV B (MassDEP EPH)

Parameter	Required Analytical Deliverable
GC Performance	***NO***
Retention Time Windows	***NO***
Initial Calibration	***NO***
Initial Calibration Verification	***NO***
Continuing Calibration (CCAL)	***NO***
Method Blank	***YES***
Laboratory Control Samples (LCSs)	***YES***
LCS Duplicates	***YES***
Matrix Spike (MS)	***YES (if requested by data user)***
Matrix Spike Duplicate (MSD)	***YES (if requested by data user)***
Matrix Duplicate (MD)	***YES (if requested by data user)***
Extraction Surrogates	***YES***
Fractionation Surrogates	***YES***
Fractionation Check Standard	***NO***
GC/MS QC Parameters	***YES (GC/MS only)*** ***See WSC-CAM II B, Table II B-1***
Identification and Quantitation	***NO***
General Reporting Issues	***YES***

3.2.1 Sample Dilution

Under circumstances that sample dilution is required because either the concentration of one or more of the target analytes or hydrocarbon ranges exceed the concentration of their respective highest calibration standard or any non-target peak exceeds the dynamic range of the detector (i.e., “off scale”), the RL for each target analyte or hydrocarbon range must be adjusted (increased) in direct proportion to the Dilution Factor (DF).

The revised RL for the diluted sample, RL_d:

$$RL_d = DF \times \text{Lowest Calibration Standard for Target Analyte}$$

It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy MCP standards/criteria 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 and hydrocarbon ranges which exceed the calibration range. All dilutions must be fully documented in the laboratory narrative.

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

Appendix IV B-1

Sample Collection, Preservation, and Handling Procedures for Extractable Petroleum Hydrocarbon Analyses

Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for EPH analyzed in support of MCP decision-making are summarized below and presented in Appendix VII A-1 of WSC-CAM-VII A, *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data Conducted in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)*.

Matrix	Container[1]	Preservation[6]	Holding Time[3,5]
Aqueous Samples	(2) 1-L amber glass bottles w/ Teflon-lined screw caps	1:1 HCl to pH <2; Cool to ≤ 6°C but not frozen	14 days to extraction; 40 days from extraction to analysis[4]
Soil/Sediment Samples	4-oz. (120 mL) wide-mouth amber glass jar with Teflon-lined screw cap[2]	Cool to ≤ 6°C but not frozen [2]	14 days to extraction; 40 days from extraction to analysis[2,4]
Waste Samples	Collect sample in one (1) x 500 mL amber wide mouth jar with a teflon-lined screw cap.	No special preservation required	14 days to extraction; 40 days from extraction to analysis[4]

[1]The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis.

[2]Alternatively, soil/sediment samples for EPH analyses may be held for up to one (1) year if frozen within 24 hours of collection at <-10°C. Sampling container should only be filled to 2/3 of capacity to avoid breakage caused by expansion during freezing. Preparation or extraction must be commenced within 24 hours of thawing. Temperature must never be allowed to go below –20°C to avoid damage to seals, etc.

[3]Holding time begins from time of sample collection or date thawed (see note #2 above).

[4]EPH sample extracts must be stored at 4°C, protected from light, and stored in sealed vials (e .g., screw-cap or crimp-capped vials) with un-pierced PTFE-lined septa.

[5]As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, September 2007, if the holding time is exceeded by >2x the allowable holding time, data users should consider nondetect results as unusable and positive results as estimated with a significantly low bias.

[6]If samples were received by the laboratory on the same day of collection and were stored and transported to the laboratory on ice, cooler temperatures above 6ºC are acceptable.

Appendix IV B-2

Data Deliverable Requirements for Data Audits

If requested by MassDEP, submission of the information listed below may be required to perform a data audit to verify compliance with the analytical methods and to evaluate accuracy and reliability of the reported results. These deliverables represent a "full data package" including all sample documentation from receipt through preparation, analysis, and data reporting. The laboratory must ensure that these deliverables are available, in the event a data audit is performed. The laboratory is required to retain these deliverables for a period of 10 years from the date generated.

DELIVERABLE REQUIREMENTS FOR DATA AUDITS WSC-CAM-IV B (EPH)	
Laboratory Narrative	Must comply with the required laboratory narrative contents as described in WSC-CAM-VII A
Sample Handling Information	Chains-of-custody (external and internal), sample receipt logs (cooler temperatures and sample pH), correspondences
Miscellaneous Logs	Dry weight logs Injection logs Soil/sediment sample weight logs Freezer logs Sample preparation/cleanup logs[1]
Initial Calibration Data	Summary of calibration factors for all standards in initial calibration; average calibration factors, %RSDs, correlation coefficients, and coefficients of determination for all target compounds Chromatograms for all standards used in initial calibration clearly showing integration of ranges and target PAHs Quantitation reports for all standards used in initial calibration Concentrations of standards used must be clearly presented Demonstration of absence of mass discrimination (i.e., acceptable C_{28}/C_{20} ratio) in all aliphatic calibration standards Demonstration of adequate resolution of naphthalene and dodecane in the aliphatic calibration standards
Initial Calibration Verification Data	Summary of percent recoveries for all target compounds Chromatograms for all ICVs clearly showing integration of ranges and target PAHs Quantitation reports for all ICVs Concentrations of standard used must be clearly presented
Continuing Calibration Data	Summary of %Ds and calibration factors Chromatograms for all continuing calibration standards clearly showing integration of ranges and target PAHs Quantitation reports for all continuing calibration standards Concentrations of standards used must be clearly presented Demonstration of absence of mass discrimination (i.e., acceptable C_{28}/C_{20} ratio) in all aliphatic calibration standards

DELIVERABLE REQUIREMENTS FOR DATA AUDITS WSC-CAM-IV B (EPH)	
	Demonstration of adequate resolution of naphthalene and dodecane in the aliphatic calibration standards
Sample Results	Chromatograms for all sample analyses, reanalyses, and dilutions clearly demonstrating how hydrocarbon ranges, target PAHs, and surrogates were integrated Quantitation reports for all sample analyses, reanalyses, and dilutions Percent solids results Summary of results, including reporting limits for each sample Date of analysis
Method Blank Results	Chromatograms for all method blanks Quantitation reports for all method blanks Summary of results, including reporting limits Summary of how method blank was prepared in solid and aqueous matrices, as appropriate
LCS/LCS Duplicate Results	Chromatograms for all LCS and LCS Duplicates Quantitation reports for all LCS and LCS Duplicates clearly showing area counts of naphthalene and 2-methylnaphthalene as well as other target analytes Summary of results, including concentrations detected, concentrations spiked, percent recoveries, percent breakthrough of naphthalene and 2-methylnaphthalene and RPDs Summary of how LCS/LCS Duplicates were prepared in solid and aqueous matrices, as appropriate
MS/MSD Results (if performed)	Chromatograms for all MS/MSDs Quantitation reports for all MS/MSDs Summary of results, including unspiked sample concentrations, concentrations detected, concentrations spiked, percent recoveries and RPDs Summary of how MS/MSDs were prepared in solid and aqueous matrices, as appropriate
Fractionation Check Standard	Chromatograms for all fractionation check standards Quantitation reports for all fractionation check standards Summary of fractionation check standard results including the concentrations detected, the concentrations spiked, and the percent recoveries
QC Summaries (both columns)	Extraction and fractionation surrogate recoveries Volume of fractionation surrogate added to extracts Internal standard performance Retention time windows Results of GC/MS analyses of blank contaminants if blank

DELIVERABLE REQUIREMENTS FOR DATA AUDITS WSC-CAM-IV B (EPH)	
	subtraction used Fractionation procedure used Injection volume of extracts
Other Information	Demonstration that ICV, LCS, and MS/MSD prepared from second source standard Chromatograms of system solvent blanks and total area counts of hydrocarbon ranges, if baseline correction is used
Additional Information Required When GC/MS Analysis is Utilized	DFTPP tunes: raw data, tune summaries, mass spectrum Internal standard area count summaries for all samples, standards, and QC samples Mass spectra of all positive target PAH results
Quantitation reports must exhibit peak area counts or peak heights, as appropriate, of target compounds, internal standards, and surrogates. [1]Must clearly indicate sample weights or volumes, final extract volumes, extraction method used, extraction times where appropriate for the method, etc.	

Appendix IV B-3

Flow Charts Describing the EPH Method Analytical Process

Exhibit IV B-1 **EPH Method Aqueous Extraction Process**

Exhibit IV B-2 **EPH Method Soil/Sediment Extraction Process**

Exhibit IV B-3 **EPH Method Fractionation Process**

Exhibit IV B-4 **EPH Method Analysis and Quantitation Process**

Exhibit IV B-1 - EPH Method Aqueous Extraction Process

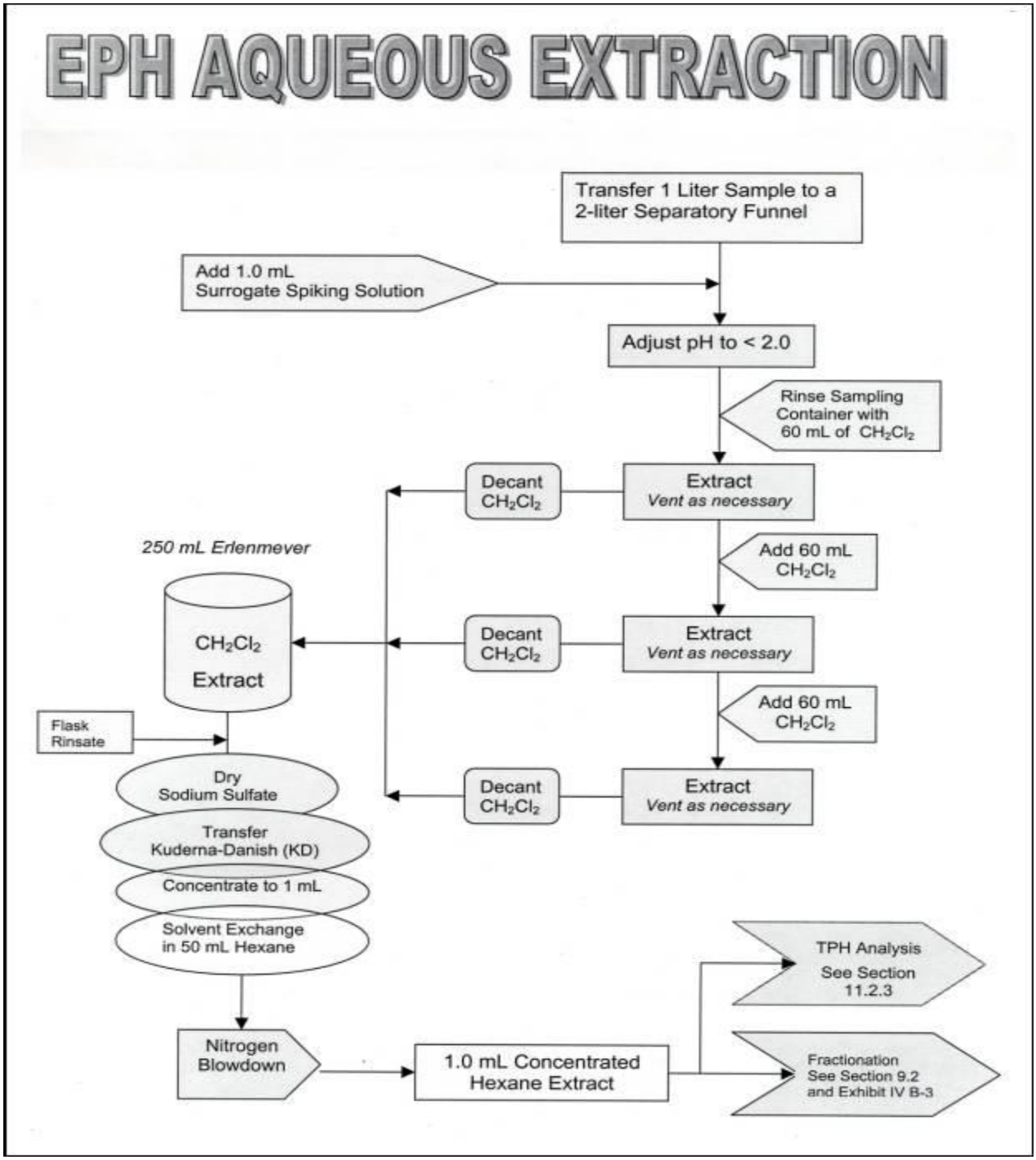


Exhibit IV B-2 – EPH Method Soil/Sediment Extraction Process

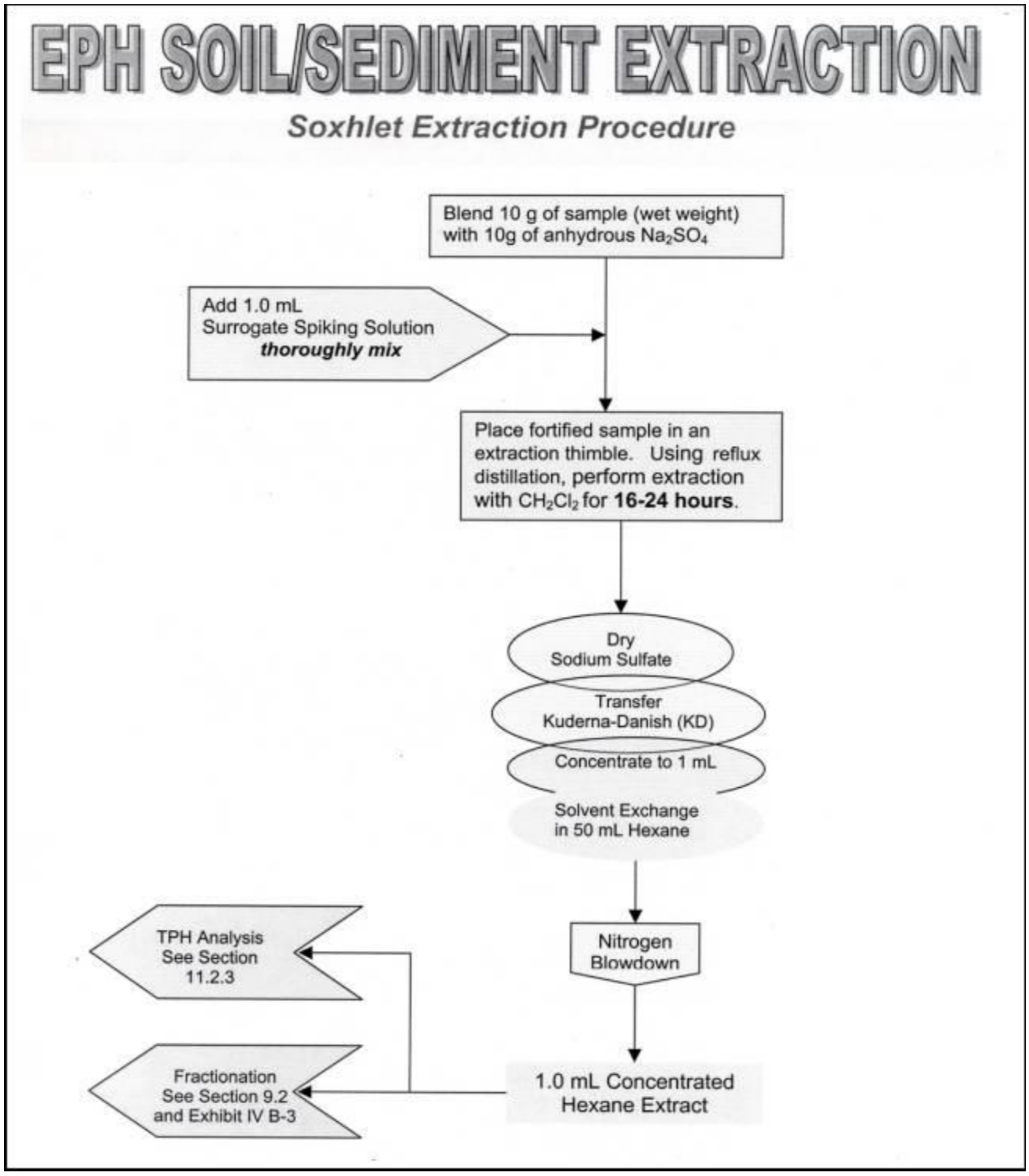


Exhibit IV B-3 - EPH Method Fractionation Process

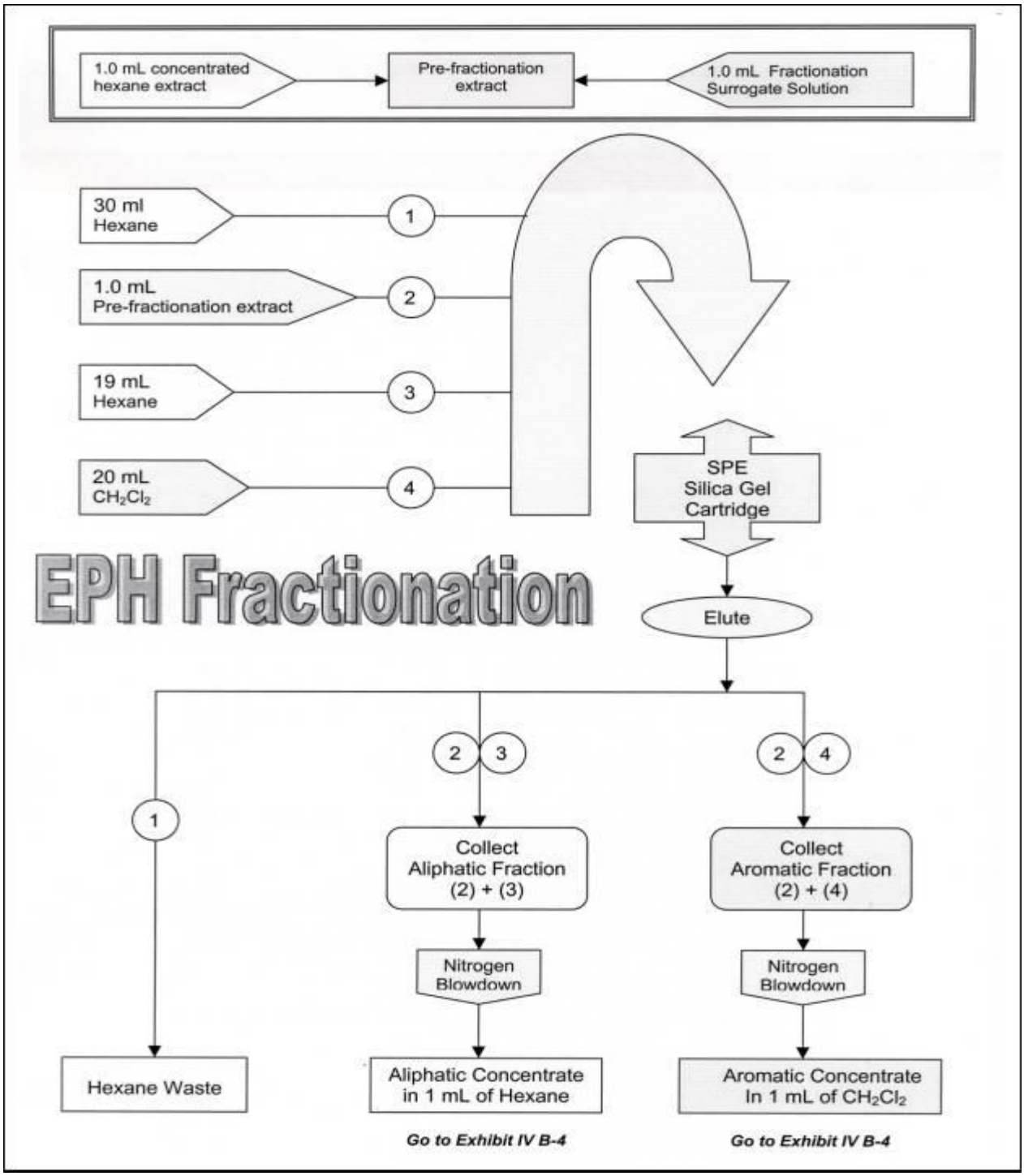


Exhibit IV B-4 - EPH Method Analysis and Quantitation Process

