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Quality Control Requirements and Performance Standards for the <i>Analysis of Volatile Petroleum Hydrocarbons (VPH) by Gas Chromatography/Photoionization Detector/Flame Ionization Detector</i> in Support of Response Actions under the Massachusetts Contingency Plan (MCP)			

WSC – CAM – IV A

Quality Control Requirements and Performance
Standards for the ***Analysis of Volatile Petroleum
Hydrocarbons (VPH) by Gas
Chromatography/Photoionization Detector/Flame
Ionization Detector*** in Support of Response Actions
under the Massachusetts Contingency Plan (MCP)

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IV. Petroleum Hydrocarbon Methods


A. Quality Control Requirements and Performance Standards for WSC-CAM-IV A (Volatile Petroleum Hydrocarbons [VPH] by GC/PID/FID)

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ACRONYM LIST

CAM	Compendium of Analytical Methods	MTBE	Methyl tertiary butyl ether
CASN	Chemical Abstracts Service Number	NA	Not applicable
CCAL	Continuing calibration	PID	Photoionization detector
%D	Percent difference or percent drift	QA	Quality assurance
DF	Dilution factor	QC	Quality control
FID	Flame ionization detector	r	Correlation coefficient
GC	Gas chromatograph	r²	Coefficient of determination
GC/MS	Gas chromatography/mass spectrometry	RCs	Reportable Concentrations
HCl	Hydrochloric acid	RL	Reporting limit
ICV	Initial calibration verification	RPD	Relative percent difference
IRAs	Immediate Response Actions	RQs	Reportable Quantities
LCS	Laboratory control sample	%R	Percent recovery
MassDEP	Massachusetts Department of Environmental Protection	%RSD	Percent relative standard deviation
MCP	Massachusetts Contingency Plan	SIM	Selective ion monitoring
MD	Matrix duplicate	TPH	Total petroleum hydrocarbons
MGP	Manufactured gas plant	TSP	Trisodium phosphate dodecahydrate
mL	milliliter	UCM	Unresolved complex mixture
MOHML	Massachusetts Oil and Hazardous Materials List	µg/kg	micrograms per kilogram
MS	Matrix spike	µg/L	micrograms per liter
MSD	Matrix spike duplicate	VOC	Volatile organic compound
		VPH	Volatile petroleum hydrocarbons

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

1.1 Overview of WSC-CAM-IV A

WSC-CAM-IV A, *Quality Control Requirements and Performance Standards for the Analysis of Volatile Petroleum Hydrocarbons by Gas Chromatography/Photoionization Detector/Flame Ionization Detector in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*, is a component of MassDEP's Compendium of Analytical Methods (CAM). Effective June 1, 2018, this revised CAM protocol, WSC-CAM-IV A, replaces revision 1.0 of the Volatile Petroleum Hydrocarbons (VPH) CAM document, WSC-CAM-IV A (effective date, July 1, 2010). Refer to WSC-CAM-I A for an overview of the CAM process. Please note that this protocol must be followed on and after the effective date of June 1, 2018 for the purpose of "Presumptive Certainty."


MassDEP has developed and published two analytical testing methods to quantify the concentrations of VPH in aqueous and solid matrices. The first VPH method, which is the subject of this document, was issued in 1998 and involves the use of in-series photoionization and flame ionization detectors (PID and FID). It is hereafter referred to as the "VPH by GC/PID/FID" method. The second method was issued in January 2017 and involves the use of a mass spectrometer. It is hereafter referred to as the "VPH by GC/MS method."

This document provides Quality Control (QC) requirements and performance standards to be used in conjunction with MassDEP VPH by GC/PID/FID Method Revision 2.1, February 2018, for the analysis of VPH in aqueous and solid (soil and sediment) samples by GC/PID/FID. The QC requirements and performance standards specified in this document in Table IV A-2 together with the analytical procedures described in the MassDEP Method constitute the WSC-CAM-IV A 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 VPH by GC/PID/FID method is a "Presumptive Certainty" requirement of WSC-CAM-IV A.

Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for VPH analyzed in support of MCP decision-making are presented in Appendix IV A-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)*. Note that these requirements are identical for both VPH methods (i.e., VPH by GC/PID/FID and VPH by GC/MS).

Data reporting requirements for the VPH by GC/PID/FID method are also provided in Section 3.2 of the CAM protocol and WSC-CAM-VIIA.

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*.

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1.1.1 Reporting Limits for WSC-CAM-IV A

The reporting limit (RL) for an individual compound using WSC-CAM-IV A 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, percent solids, dilution factors, etc., as required. The CAM RLs for WSC-CAM-IV A target analytes and hydrocarbon ranges are:

- 50-250 µg/kg (wet weight) for VPH target analytes in soil/sediment samples (assuming 100% solids);
- 5,000-10,000 µg/kg (wet weight) for each hydrocarbon range in soil/sediment samples (assuming 100% solids);
- 1-5 µg/L for VPH target analytes in aqueous samples (surface water, groundwater, and drinking water); and
- 100-150 µg/L for each hydrocarbon range in aqueous samples (surface water, groundwater, and drinking water).


These values are readily achievable using GC/PIDs/FIDs. For “Presumptive Certainty” purposes, if the CAM RLs are not achieved, a “NO” response to Question G of the “MassDEP MCP Analytical Protocol Certification Form” is required and the CAM RL exceedance must be addressed in the laboratory narrative.

Reporting limits lower than the above-referenced CAM RLs for WSC-CAM-IV A 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, etc.). Meeting MCP standards or criteria for VPH target analytes may require analytical 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 A VPH target analytes and hydrocarbon ranges will be proportionately higher for samples that require dilution or when a reduced sample size is used.

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

Each laboratory that uses the WSC-CAM-IV A 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 (MD) 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 A-2 of this protocol. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in the MassDEP VPH by GC/PID/FID method (Section 10.5 and Appendix 7). The data associated with the Initial Demonstration of Proficiency must be kept on file at the

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laboratory and made available to potential data users on request. The data associated with the Initial Demonstration of Proficiency for WSC-CAM-IV A must include the following information:

QC Element	Performance Criteria
Initial Calibration	WSC-CAM-IV A, Table IV A-2
Continuing Calibration	WSC-CAM-IV A, Table IV A-2
Method Blanks	WSC-CAM-IV A, Table IV A-2
Average Recovery	MassDEP VPH by GC/PID/FID Method, Appendix 7, Section 3
% Relative Standard Deviation	MassDEP VPH by GC/PID/FID Method, Appendix 7, Section 4
Surrogate Recoveries	WSC-CAM-IV A, Table IV A-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 8000D, Section 9.6. 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 A-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 A protocol, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table IV A-2. It should be noted that the performance standards listed in Table IV A-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/PID/FID instrumentation as a quantitative tool and skilled in the interpretation of chromatograms for individual target analytes and petroleum hydrocarbon ranges.

1.2 Summary of MassDEP VPH by GC/PID/FID Method

Volatile compounds are introduced into the gas chromatograph using a purge-and-trap concentrator as described in SW-846 methods 5030B and 5035A for aqueous and solid samples, respectively. The analytes are then introduced directly to a capillary column for analysis. The GC oven is temperature-programmed to facilitate separation of the target analytes and hydrocarbon ranges of interest which are then detected using a

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PID and FID, that are interfaced directly to the GC, operating in series. The resultant chromatogram of aliphatic compounds is collectively integrated within the C₅ through C₈ and C₉ through C₁₂ ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C₉ through C₁₀ range, and is (optionally) used to identify and quantify individual concentrations of VPH target analytes. Identification of VPH target analytes is accomplished by comparing the sample retention time with the retention time of standards obtained under identical analytical conditions.

Average calibration factors (or calibration curves) determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of C₅ through C₈ and C₉ through C₁₂ aliphatic hydrocarbons from the FID. An average calibration factor (or calibration curve) determined using an aromatic standard mixture is used to calculate a collective concentration of C₉ through C₁₀ aromatic hydrocarbons from the PID. Calibration factors (or calibration curves) are also used to calculate individual concentrations of Target VPH Analytes. The VPH method marker compounds and retention time windows are summarized in Table IV A-1.

Table IV A-1: VPH Method Range Marker Compounds		
Hydrocarbon Range	Beginning Marker Compound	Ending Marker Compound
C ₅ -C ₈ Aliphatic Hydrocarbons	0.1 minutes before n-pentane	0.01 minutes before n-nonane
C ₉ -C ₁₂ Aliphatic Hydrocarbons	0.01 minutes before n-nonane	0.1 minutes before naphthalene
C ₉ -C ₁₀ Aromatic Hydrocarbons	0.1 minutes after o-xylene	0.1 minutes before naphthalene


1.3 Sample Preparation Methods for WSC-CAM-IV A

- Analysis of Aqueous Samples

Aqueous samples may be analyzed directly without sample preparation. The analysis of aqueous samples is described in detail in Section 9.1.2 of the VPH by GC/PID/FID Method. In general, a sample aliquot is introduced to the purge chamber. If necessary, samples may be diluted prior to injection into the purge chamber.

- Analysis of Soil and Sediment Samples

Soil and sediment samples are dispersed in methanol to extract the volatile petroleum hydrocarbons. A portion of the methanol extract is then extracted/concentrated by purge-and-trap and analyzed by GC/PID/FID. Methanol may be added in the field or in the laboratory if the samples are collected in specially designed air-tight samplers. The desired ratio of methanol-to-soil is 1 mL methanol/1 gram soil, ± 25%. Highly-organic matrices (e.g., peat) may require additional methanol (up to 2 mL per gram of soil). In either case, an aliquot of the methanol extract is added to reagent water and introduced into the GC/PID/FID using a purge-and-trap concentrator. The volume of the methanol aliquot will depend on the anticipated VPH concentration. Refer to Section 9.1.3 of the VPH by GC/PID/FID Method for details on analyzing soil/sediment samples. ***Be advised that the volume of methanol aliquot added to the reagent water should not exceed 200 µL to preclude adverse solvent front and trap breakthrough difficulties.***

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1.4 Method Interferences

- Refer to SW-846 Method 8260B for a detailed description of chemical contaminants, cross-contamination, and corrective actions which may be taken to eliminate contamination. If a method blank contains a contaminant, data for samples associated with that blank must **not** undergo “blank correction” (i.e., if an associated sample also contains the contaminant, subtraction of the blank amount from the sample amount is not permitted).

Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of VPH. After the analysis of a sample containing high concentrations of VPH, one or more blanks should be analyzed to check for potential cross-contamination/carryover. Concentrations of target VPH analytes 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.

- Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container’s septum during shipment and storage. A trip blank carried through sampling and subsequent storage and handling can serve as a check on such contamination.

1.5 Quality Control Requirements for WSC-CAM-IV A

1.5.1 General QC Requirements


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

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

Specific QC requirements and performance standards for the WSC-CAM-IV A protocol are presented in Table IV A-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:

- Use the analytical method specified for the selected CAM protocol;
- Incorporate **all** required analytical QC elements specified for the selected CAM protocol;
- Implement, as necessary, required corrective actions and analytical response actions for **all** non-conforming analytical performance standards;
- Evaluate and narrate, as necessary, **all** identified CAM protocol non-compliances; and

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- (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) and 40.1057(2)(k) for Permanent and Temporary Solution submittals, respectively, 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 A


The following bullets highlight potential issues that may be encountered with the analysis of VPH by GC/PID/FID using this protocol.

- Petroleum products suitable for evaluation by this method include gasoline, mineral spirits, and certain petroleum naphthas. The VPH by GC/PID/FID Method, in and of itself, is not suitable for the evaluation of kerosene, jet fuel, heating oils, lubricating oils, or other petroleum products, that contain higher boiling components or distillates of aliphatic and/or aromatic hydrocarbons that are outside the aforementioned analytical range (C_9 through C_{12} aliphatic and aromatic ranges) of the MassDEP VPH by GC/PID/FID Method.
- Although procedures for manual purge-and-trap load systems are provided in the Mass DEP VPH by GC/PID/FID Method, MassDEP prefers the use of purge-and-trap autosamplers to reduce variability and to minimize the handling of samples for VPH analysis.
- When analyzing aqueous samples for methyl tertiary butyl ether (MTBE), samples should not be preserved with acid if heated purge-and-trap ($>40^{\circ}\text{C}$) is used as the sample introduction method. See Appendix II A-1 for the preferred preservation technique under this condition. However, it should be noted that the use of heated purge ($>40^{\circ}\text{C}$) is considered a "significant modification" of the VPH by GC/PID/FID method and must be disclosed in the laboratory narrative.
- The recovery of matrix spikes from a soil/sediment sample that has been preserved with methanol cannot be used to directly evaluate matrix-related bias/accuracy in the conventional definition of these terms. QC parameters expressed in terms of these percent recoveries (%R) may be more indicative of the variabilities associated with the analytical system (sample processing, introduction, and/or component separation). This inherent limitation of methanol preservation with respect to the evaluation of matrix spike recoveries is more than compensated for by the marked improvement in sample integrity and conservation/recoveries of the VPH analytes of concern from soil/sediment matrices by minimizing volatilization losses.
- Both VPH target 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

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recommended in cases where a Target VPH Analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where co-elution of a 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 VPH analyte.
 - Compounds not meeting the regulatory definition of the aromatic and/or aliphatic fractions as defined in Sections 3.6, 3.7 and 3.8 of the VPH by GC/PID/FID Method that elute within the method-defined retention time window would be included in the total area and thus the result would 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.
 - Although not a predominant component in petroleum hydrocarbon mixtures, alkenes and other non-aromatic hydrocarbons can elicit a positive PID response. In general, the PID response to these non-aromatic compounds is weaker than the response for the same mass of an aromatic hydrocarbon. However, at elevated concentrations, these non-aromatic compounds may interfere or yield false positives (high positive bias) for Target VPH Analytes or aromatic hydrocarbon range concentrations.
- In general, it may be prudent to confirm all PID/FID data using SW-846 Method 8260B (GC/MS) if critical MCP decision-making (notification, compliance with cleanup standards, risk assessment, etc.) is based solely on the VPH by GC/PID/FID Method (or any other non-specific GC analysis). If a positive interference is suspected from hydrocarbons and/or non-hydrocarbons not associated with VPH in either the aliphatic or the aromatic fraction or with a Target VPH Analyte, and such interference could adversely affect MCP decision-making, then SW-846 Method 8260B, WSC-CAM-II A, Volatile 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.
 - The VPH by GC/PID/FID Method should be used with caution at sites with an uncertain history, particularly closed or abandoned Manufactured Gas Plants (MGPs). Styrene, a common contaminant of concern at many MGP sites, cannot be satisfactorily resolved from o-xylene under the chromatographic conditions specified for the VPH by GC/PID/FID Method. If encountered, co-eluting styrene could cause an overestimation of o-xylene. Other contaminant pairs routinely encountered at MCP sites that are difficult to resolve under the chromatographic conditions specified for the VPH by GC/PID/FID method include 1,2-dichloroethane/benzene and 1,1,1,2-tetrachloroethane/ethylbenzene.
 - Be advised that any adaptation to the VPH by GC/PID/FID Method that constitutes a "significant modification" pursuant to Section 11.3.1 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 VPH by GC/PID/FID Method analytical report form, as described in Section 11.3 and Appendix 3 of the VPH by GC/PID/FID 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)

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requirements specified in Table IV A-2. Experience has shown that %RSD requirements are easily achievable for Target VPH Analytes; linear regression may be occasionally required for one or more hydrocarbon ranges. Non-linear regression should not be required for this method and is considered a “significant modification” pursuant to Section 11.3.1 and will preclude obtaining “Presumptive Certainty” status for any analytical data produced using such modification.



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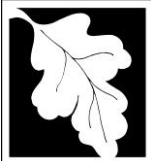
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Table IV A-2: Specific QC Requirements and Performance Standards for Volatile Petroleum Hydrocarbons (VPH) by GC/PID/FID Using WSC-CAM-IV A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350 ¹	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 aliphatic and aromatic hydrocarbon standards listed in Table 1 of the VPH by GC/PID/FID method. (4) Must follow procedure in Appendix 7 of the VPH by GC/PID/FID method.	No	NA	Refer to Appendix 7 of the VPH by GC/PID/FID method and Section 1.1.2 of this protocol.	NA
GC Performance	Inter-laboratory Consistency and Comparability	(1) n-Pentane and MTBE must be adequately resolved from solvent front. (2) Surrogate standards must be adequately resolved from Target VPH Analytes.	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. (1) Calculated according to the method (Section 9.3). (2) Retention time windows must be updated with every continuing calibration.	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 20 for Target VPH Analytes and \leq 25 for hydrocarbon ranges, r	No	NA	(1) Recalibrate as required by method. (2) In the case of linear or non-linear regression, if recalculated concentrations from the lowest calibration standard are outside of 70-130% recovery range, either: * The RL must be reported as an	Sample analysis cannot proceed without a valid initial calibration. If non-linear regression (i.e., quadratic equation) is used for calibration, this must be noted in the laboratory narrative along with the Target VPH Analytes or hydrocarbon ranges affected.



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Table IV A-2: Specific QC Requirements and Performance Standards for Volatile Petroleum Hydrocarbons (VPH) by GC/PID/FID Using WSC-CAM-IV A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350 ¹	Required Corrective Action	Required Analytical Response Action
		<p>≥ 0.99 (linear regression), or $r^2 \geq 0.99$ (non-linear regression) for each Target VPH Analyte and hydrocarbon range.</p> <p>(5) If %RSD >20 for Target VPH Analytes and >25 for hydrocarbon ranges, linear or non-linear regression must be used.</p> <p>(6) Must contain all aliphatic and aromatic hydrocarbon standards listed in Table 1 of the VPH by GC/PID/FID Method.</p> <p>(7) Must meet GC performance standards described in Section 10.2.1 of the VPH by GC/PID/FID method.</p> <p>(8) Calibration must be performed under the same conditions as the samples (e.g., heated purge).</p> <p>(9) If autosampler used to spike surrogates in calibration standards, a one-point calibration with 5 standards is acceptable for surrogates.</p> <p>(10) (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%.</p>			<p>estimated value², or</p> <p>* The RL must be raised to the concentration of the next highest calibration standard that exhibits acceptable recoveries when recalculated using the final calibration curve.</p>	
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	<p>(1) Immediately after each initial calibration.</p> <p>(2) Concentration level near midpoint of curve.</p> <p>(3) Prepared using standard source different than used for initial calibration.</p>	No	NA	Locate source of problem; recalibrate if >10% of all analytes are outside of criteria.	If recovery is outside of 70-130% for any Target VPH Analyte or hydrocarbon range, report non-conforming analyte or hydrocarbon range in laboratory narrative.



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Table IV A-2: Specific QC Requirements and Performance Standards for Volatile Petroleum Hydrocarbons (VPH) by GC/PID/FID Using WSC-CAM-IV A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350 ¹	Required Corrective Action	Required Analytical Response Action
		(4) Must contain all aliphatic and aromatic hydrocarbon standards listed in Table 1 of the VPH by GC/PID/FID Method. (5) Percent recoveries must be between 70-130% for each Target VPH Analyte and hydrocarbon range.				
Continuing Calibration	Laboratory Analytical Accuracy	(1) Prior to samples, every 20 samples 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 Table 1 of the VPH by GC/PID/FID method. (4) %D or % drift must be ≤ 20 for all Target VPH Analytes and ≤ 25 for hydrocarbon ranges except for n-nonane, which must be ≤ 30 . (5) Must meet GC performance standards described in Section 10.2.1 of the VPH by GC/PID/FID method. (6) Verify that all analytes fall within retention time windows.	No	NA	(1) Perform instrument maintenance, reanalyze continuing calibration and/or recalibrate as required by method. (2) Reanalyze "associated samples" if beginning or ending continuing calibration exhibited low response. (3) Reanalyze "associated samples" if beginning or ending continuing calibration exhibited high response and associated Target VPH Analytes and hydrocarbon ranges were detected in the "associated samples." NOTE: "Associated samples" refers to all samples analyzed since the last acceptable continuing calibration.	Report non-conforming Target VPH Analytes (%D >20) or hydrocarbon ranges (%D >25) and associated samples in laboratory narrative.



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Table IV A-2: Specific QC Requirements and Performance Standards for Volatile Petroleum Hydrocarbons (VPH) by GC/PID/FID Using WSC-CAM-IV A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350 ¹	Required Corrective Action	Required Analytical Response Action
Method Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Matrix and preservative-specific (e.g., water, methanol). (3) VPH 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 VPH 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-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-analysis 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-analysis is performed within holding time and yields acceptable method blank results, the laboratory may report results of the re-analysis only. (4) If re-analysis is performed outside of holding time, the laboratory must report results of both the initial analysis and re-analysis.



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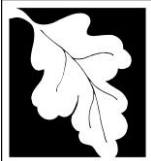
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Table IV A-2: Specific QC Requirements and Performance Standards for Volatile Petroleum Hydrocarbons (VPH) by GC/PID/FID Using WSC-CAM-IV A

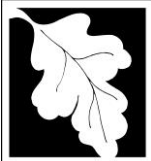
Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350 ¹	Required Corrective Action	Required Analytical Response Action
Laboratory Control Sample (LCS)	Laboratory Analytical Accuracy	(1) Analyzed with every batch or every 20 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 Table 1 of the VPH by GC/PID/FID method. (5) Matrix and preservative-specific (e.g., water, methanol). (6) Percent recoveries must be between 70-130% for Target VPH Analytes and hydrocarbon ranges.	Yes	Recovery <10%; affects results for affected analyte/hydrocarbon range in all samples analyzed with this LCS.	(1) Locate source of problem; re-analyze LCS and associated samples if Target VPH Analytes or hydrocarbon ranges are outside of criteria. (2) (2) If Target VPH Analytes or hydrocarbon ranges are above the acceptance criteria (>130%), re-analysis is not required if affected Target VPH Analytes or hydrocarbon ranges were not detected in associated samples. (3) If LCS is re-analyzed and still outside of criteria, recalibration is required.	(1) If sample re-analysis is not possible, report non-conformance in laboratory narrative. (2) If recovery is outside of 70-130% for any analyte, report non-conforming Target VPH Analytes or hydrocarbon ranges in laboratory narrative. (3) If re-analysis is performed within holding time and yields acceptable LCS results, the laboratory may report results of the re-analysis only. (4) If re-analysis is performed outside of holding time, the laboratory must report results of both the initial analysis and re-analysis.



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Table IV A-2: Specific QC Requirements and Performance Standards for Volatile Petroleum Hydrocarbons (VPH) by GC/PID/FID Using WSC-CAM-IV A

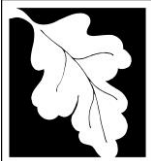
Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350 ¹	Required Corrective Action	Required Analytical Response Action
LCS Duplicate	Laboratory Analytical Accuracy & Precision	(1) Analyzed with every batch or every 20 samples, 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 Table 1 of the VPH by GC/PID/FID method. (5) Matrix and preservative-specific (e.g., water, methanol). (6) Percent recoveries must be between 70-130% for Target VPH Analytes and hydrocarbon ranges. (7) RPDs must be ≤ 25 for waters and solids.	Yes	Recovery $< 10\%$; affects results for affected analyte/hydrocarbon range in all samples analyzed with this LCS.	(1) Locate source of problem; re-analyze LCS and associated samples if Target VPH Analytes or hydrocarbon ranges are outside of recovery acceptance criteria. (2) If Target VPH Analytes or hydrocarbon ranges are above the recovery acceptance criteria ($> 130\%$), re-analysis is not required if affected Target VPH Analytes or hydrocarbon ranges were not detected in associated samples. (3) If LCS is re-analyzed and still outside of criteria, recalibration is required.	(1) If sample re-analysis is not possible, report non-conformance in laboratory narrative. (2) If recovery is outside of 70-130% or RPD > 25 for any analyte, report non-conforming Target VPH Analytes or hydrocarbon ranges in laboratory narrative. (3) If re-analysis is performed within holding time and yields acceptable LCS results, the laboratory may report results of the re-analysis only. (4) If re-analysis is performed outside of holding time, the laboratory must report results of both the initial analysis and re-analysis.
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. (4) Must contain all aliphatic and	Yes ONLY when requested by the data user	Recovery $< 10\%$; affects result for affected analyte/hydrocarbon range in unspiked sample only.	Check LCS; if recoveries are acceptable in LCS, narrate non-conformance.	Note exceedances in laboratory narrative.



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Table IV A-2: Specific QC Requirements and Performance Standards for Volatile Petroleum Hydrocarbons (VPH) by GC/PID/FID Using WSC-CAM-IV A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350 ¹	Required Corrective Action	Required Analytical Response Action
		aromatic hydrocarbon standards listed in Table 1 of the VPH by GC/PID/FID method. (5) Matrix-specific (e.g., water, methanol). (6) Percent recoveries must be between 70-130% for target analytes and hydrocarbon ranges. (7) (7) RPDs ≤50 for waters and solids.				
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., water, methanol). (3) (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 1 surrogate. Recommended surrogate: 2,5-dibromotoluene (2) Percent recoveries must be between 70-130% on PID and FID.	Yes (report recovery from PID and FID)	Recovery <10% on PID: affects all results for Target VPH Analytes and C ₉ -C ₁₀ aromatics in affected sample. Recovery <10% on FID: affects all results for C ₅ -C ₈ aliphatics and C ₉ -C ₁₂ aliphatics in affected sample.	If surrogate is outside of limits, reanalyze sample unless one of the following exceptions applies: (1) Obvious interference present (e.g., UCM). NOTE: If obvious interference is present and surrogate recovery would cause rejection of data (i.e., <10%), reanalyze sample on dilution. (2) Methanol-preserved samples: re-analysis is not required if % moisture >25 and surrogate recovery is	(1) Report recoveries outside of 70-130% in laboratory narrative. (2) If re-analysis yields similar surrogate non-conformances, the laboratory must report results of both analyses. (3) If re-analysis is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the re-analysis only. (4) If re-analysis is performed outside of



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Table IV A-2: Specific QC Requirements and Performance Standards for Volatile Petroleum Hydrocarbons (VPH) by GC/PID/FID Using WSC-CAM-IV A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350 ¹	Required Corrective Action	Required Analytical Response Action
					>10%. (3) If surrogate exhibits high recovery and associated Target VPH Analytes or hydrocarbon ranges are not detected in sample, reanalysis is not required. NOTE: Surrogate recoveries from PID affect Target VPH Analytes and C₉-C₁₀ aromatics. Surrogate recoveries from FID affect C₅-C₈ aliphatics and C₉-C₁₂ aliphatics.	the holding time and yields acceptable surrogate recoveries, the laboratory must report results of both analyses. (5) If sample is not re-analyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.
Quantitation	NA	(1) The laboratory must use the average calibration factor, linear or non-linear regression curve generated from the associated initial calibration for quantitation of each Target VPH 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". ³	NA	NA	NA	NA



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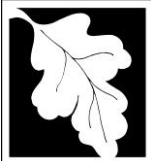
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Table IV A-2: Specific QC Requirements and Performance Standards for Volatile Petroleum Hydrocarbons (VPH) by GC/PID/FID Using WSC-CAM-IV A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350 ¹	Required Corrective Action	Required Analytical Response Action
Identification	NA	(1) Refer to Section 9.5.2 of the VPH by GC/PID/FID Method.	NA	NA	NA	NA
General Reporting Issues	NA	(1) The laboratory must only report values \geq 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 <u>each</u> Target VPH Analyte and hydrocarbon range. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported. (3) All soil/sediment sample results must be corrected for the methanol dilution as per Section 9.6.4 of the VPH by GC/PID/FID Method and Section 3.2.1 of this CAM protocol. (4) All information required in Appendix 3 of the VPH by GC/PID/FID Method must be provided for each sample in a "clear and concise manner."	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 VPH Analytes or hydrocarbon ranges, reasons for dilutions must be explained in the laboratory narrative. (3) If samples are not



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Table IV A-2: Specific QC Requirements and Performance Standards for Volatile Petroleum Hydrocarbons (VPH) by GC/PID/FID Using WSC-CAM-IV A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350 ¹	Required Corrective Action	Required Analytical Response Action
		(5) Results for soils/sediments must be reported on a dry-weight basis for comparison to MCP regulatory standards. (6) Refer to Appendix IV A-1 for chain-of-custody requirements regarding preservation, cooler temperature, and holding times. (7) The laboratory must report the GC column used (manufacturer, column name, length, ID, and film thickness). (8) The laboratory must report the trap used in the purge-and-trap system (manufacturer, trap contents).				properly preserved (pH >2 for aqueous samples, solid samples not completely covered with methanol preservative, and/or solid sample/methanol ratio outside 1:1 ±25%) or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory narrative. (4) If samples are preserved and/or analyzed outside of the holding time, note the non-conformances in the laboratory narrative.

¹As 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.

²If 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.

³Reporting 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.

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1.7 Analyte List for WSC-CAM-IV A

The MCP analyte list for WSC-CAM-IV A is presented in Table IV A-3. The list is comprised of eight (8) target analytes and three (3) collectively quantified volatile hydrocarbon ranges. Use of the VPH by GC/PID/FID Method to identify and quantify the listed VPH target 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 and hydrocarbon ranges. 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: <http://www.mass.gov/dep/cleanup/laws/regulati.htm#mcp>
- An online searchable Oil & Hazardous Materials List of RQs and RCs values may be found at the following URL: <http://public.dep.state.ma.us/momhl/hazmat.aspx>.
- An updated list of MCP Method 1 Standards may be found at the following URL: <http://www.mass.gov/eea/agencies/massdep/cleanup/regulations/mcp-numerical-standards.html>.

All of the Target VPH Analytes and hydrocarbon ranges that comprise the Analyte List for the VPH by GC/PID/FID Method have promulgated MCP Method 1 groundwater/soil standards.


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

While it is not necessary to request and report all the WSC-CAM-IV A analytes listed in Table IV A-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.

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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 A to obtain “Presumptive Certainty” status.

Table IV A-3: Analyte List for WSC-CAM-IV A (MassDEP VPH by GC/PID/FID)	
Analyte	CASN
VPH Ranges:	
C ₅ -C ₈ Aliphatic Hydrocarbons	NA
C ₉ -C ₁₂ Aliphatic Hydrocarbons	NA
C ₉ -C ₁₀ Aromatic Hydrocarbons	NA
VPH Target Analytes:	
Benzene	71432
Ethylbenzene	100414
Methyl-tert-butylether (MTBE)	1634044
Naphthalene	91203
Toluene	108883
o-Xylene ²	95476
m- Xylene ^{1,2}	108383
p- Xylene ^{1,2}	106423
CASN – Chemical Abstracts Service Numbers NA – Not Applicable ¹ May not be resolvable under chromatographic conditions required by this method. ² May be reported and evaluated as mixed isomers.	

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2.0 Data Usability Assessment

Specific guidance applicable to all Permanent and Temporary Solutions, including Permanent and Temporary Solutions on a portion of a disposal site, for preparation of Representativeness Evaluations and Data Usability Assessments pursuant to 310 CMR 40.1056(2)(k) and 40.1057(2)(k), respectively, 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 a Permanent or Temporary Solution submittal. The most current version of this document may be found at the following URL: <http://www.mass.gov/dep/cleanup/laws/policies.htm#finpol>

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 A

3.1 General Reporting Requirements for WSC-CAM-IV A

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 A

Specific QC requirements and performance standards for WSC-CAM-IV A are presented in Table IV A-2. Specific reporting requirements for WSC-CAM-IV A are summarized below in Table IV A-4 as “Required Analytical Deliverables”. Requirements listed as “**YES**” must always be included as part of the laboratory deliverable for this method. It should be noted that data for those items listed as “**NO**” under “Required Analytical Deliverables” must be available for review during an audit and may also be requested for inclusion in the analytical deliverable 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.



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**Table IV A-4 Routine Reporting Requirements for WSC-CAM-IV A
(MassDEP VPH by GC/PID/FID)**

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)
Surrogates	YES
Identification and Quantitation	NO
General Reporting Issues	YES


3.2.1 Data Correction for VPH Concentrations Due To Methanol Preservation Dilution Effect

VPH analytical results for soil/sediment samples must be corrected by the laboratory for the methanol preservation dilution effect. If this correction is neglected, the potential for under reporting volatile organic concentrations is more pronounced as the “as-received” % moisture content of the soil/sediment sample increases.

VPH concentrations and the recovery of matrix spikes and/or surrogates in solid samples preserved with methanol are subject to a systematic negative bias if the potential increase of the total solvent volume, as a consequence of the moisture content of the sample, is not considered. The total solvent volume is the additive sum of the volume of methanol and the sample moisture content that partitions into the methanol. The total solvent/water volume (V_t) is calculated using the following equation:

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

This “corrected” V_t value should be substituted directly for the V_t value in the equation shown in Section 9.6.2 of the VPH by GC/PID/FID Method and SW-846 Method 8000D, Sections 11.10.2 and 11.10.3. It should be noted that whether corrected or uncorrected, the V_t value used to calculate VPH concentrations must also take into consideration the volume of any surrogate/spiking solution added to soil/sediment samples.

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3.2.2 Sample Dilution


Under circumstances that sample dilution is required because either the concentration of one or more of the Target VPH 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 VPH 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 :

$$RL_d = DF \times \text{Lowest Calibration Standard for Target VPH Analyte/Hydrocarbon Range}$$

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 VPH 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 VPH Analyte/hydrocarbon range 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 VPH Analytes/hydrocarbon ranges which did not require dilution.

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Appendix IV A-1

Sample Collection, Preservation, and Handling Procedures for Volatile Petroleum Hydrocarbon by GC/PID/FID Analyses

Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for VPH 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)*.



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Matrix	Container ¹	Preservation ⁶	Holding Time ^{3,5}
Aqueous Samples (using ambient temperature purge)	3 x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light	Adjust pH to < 2.0 by addition of HCl to container before sampling. Cool to ≤ 6°C but not frozen.	14 days
Aqueous Samples (using heated purge [>40°C]) ²	3 x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light	0.4 to 0.44 g of trisodium phosphate dodecahydrate (TSP) per 40 mL. Verify pH >11.0. Cool to ≤ 6°C but not frozen.	14 days
Soil/Sediment Samples	Extrude soil/sediment sample directly into a pre-weighed vial* w/ Teflon-lined septa screw caps: Vials must contain 1 mL purge-and-trap grade methanol for every gram soil/sediment. *(1) x 60-mL vial or (1) x 40-mL vial	1 mL methanol for every gram soil/sediment; add methanol before or at time of sampling; methanol must cover soil/sediment sample Cool to ≤ 6°C but not frozen. 60-mL vial: 25g soil/sediment and 25 mL methanol 40-mL vial: 15g soil/sediment and 15 mL methanol	28 days
	5 g EnCore™ samplers ⁴ or other suitable coring device	Cool to ≤ 6°C (but not frozen) in field; 48 hours from date collected until methanol preservation (1 mL methanol for every gram soil/sediment).	28 days

¹The 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.

²Heated purge (>40°C) is considered a significant modification to the method, as per Section 11.3.1 of the VPH by GC/PID/FID method.

³Holding time begins from time of sample collection.

⁴EnCore™ sampler may not be suitable for certain soil types; refer to guidance in SW-846 Method 5035A.

⁵As 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 or if soil/sediment samples are not properly preserved, 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 6°C are acceptable.



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Additional Sample Handling and Preservation Notes:

Aqueous Samples:

1. If effervescence occurs upon addition of HCl, samples should be collected without the acid preservative. In such cases, the analysis holding time is seven (7) days from date collected to date analyzed; however, there is still a potential for a low bias that must be included in the data usability evaluation. To reduce the potential for low bias, analysis within 24 hours is recommended.


Solid Samples:

1. Samples may be collected in a hermetically sealed sampling device, such as an EnCore™ sampler. EnCore™ samplers may not be suitable for certain soil types; refer to guidance in SW-846 Method 5035A. The laboratory must transfer the contents of the EnCore™ sampler to a pre-weighed vial and preserve the sample in methanol within 48 hours of sample collection. The sample must be analyzed within 28 days of sample collection. The EnCore™ samplers must be kept at $\leq 6^{\circ}\text{C}$ from time of collection to time of preservation. The preserved samples must be kept at $\leq 6^{\circ}\text{C}$ from time of preservation until the time of analysis.
2. An extra aliquot of sample must be collected in a 4 oz. glass jar with no preservative so that the laboratory can perform a percent solids analysis. If the same sample is being submitted to the laboratory for additional analyses, which require no preservative, the percent solids analysis can be measured using an aliquot from these bottles. Otherwise, a separate bottle will be needed.

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Appendix IV A-2

Data Deliverable Requirements for Data Audits

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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 A (VPH by GC/PID/FID)	
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
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 VPH Analytes/hydrocarbon ranges Chromatograms for all standards used in initial calibration clearly showing integration of hydrocarbon range components and Target VPH Analytes Quantitation reports for all standards used in initial calibration Concentrations of standards used must be clearly presented Demonstration of adequate resolution of MTBE and n-pentane from the methanol peak in calibration standards
Initial Calibration Verification Data	Summary of percent recoveries for all Target VPH Analytes/hydrocarbon ranges Chromatograms for all ICVs clearly showing integration of hydrocarbon range components and Target VPH Analytes 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 hydrocarbon range components and Target VPH Analytes Quantitation reports for all continuing calibration standards Concentrations of standards used must be clearly presented Demonstration of adequate resolution of MTBE and n-pentane from the methanol peak in calibration standards
Sample Results	Chromatograms for all sample analyses, reanalyses, and dilutions clearly demonstrating how hydrocarbon ranges, Target VPH Analytes, and surrogates were integrated



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DELIVERABLE REQUIREMENTS FOR DATA AUDITS

WSC-CAM-IV A (VPH by GC/PID/FID)

	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 Summary of results, including concentrations detected, concentrations spiked, percent recoveries, 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
QC Summaries (both columns)	Surrogate recoveries Volume of surrogate added to methanol extracts Retention time windows
Other Information	Demonstration that ICV, LCS, and MS/MSD prepared from second source standard Volume of surrogate added to methanol extracts GC column used (manufacturer, column name, length, inside diameter, film thickness) Trap used (manufacturer, trap contents)
Additional Information Required When GC/MS Analysis is Utilized	BFB tunes: raw data, tune summaries, mass spectrum Internal standard area count summaries for all samples, standards, and QC samples Mass spectra of all positive results for Target VPH Analytes in field and QC samples

Quantitation reports must exhibit area counts or peak heights, as appropriate, of Target VPH Analytes, hydrocarbon ranges, internal standards, and surrogates.