WSC – CAM – IX A

Quality Control Requirements and Performance Standards for the ***Analysis of Air-Phase Petroleum Hydrocarbons (APH) by Gas Chromatography/Mass Spectrometry (GC/MS)*** in Support of Response Actions under the Massachusetts Contingency Plan (MCP)

IX. Air Sampling Methods

A. Quality Control Requirements and Performance Standards for WSC-CAM-IX A (Air-Phase Petroleum Hydrocarbons by GC/MS)

Table of Contents

List of Tables and Appendices

ACRONYNM LIST

APH	**Air-phase petroleum hydrocarbons**	**MD**	**Matrix duplicate**
BFB	**Bromofluorobenzene**	**NA**	**Not applicable**
CAM	**Compendium of Analytical Methods**	**NIST**	**National Institute of Standards and Technology**
CASN	**Chemical Abstracts Service Number**	**ppbV**	**Parts per billion by volume**
COC	**Chain-of-custody**	**QA**	**Quality assurance**
%D	**Percent difference or percent drift**	**QC**	**Quality control**
DF	**Dilution factor**	**r**	**Correlation coefficient**
GC	**Gas chromatograph**	**r^2**	**Coefficient of determination**
GC/MS	**Gas chromatography/mass spectrometry**	**RL**	**Reporting limit**
ICV	**Initial calibration verification**	**RPD**	**Relative percent difference**
in. Hg	**Inches of mercury**	**%RSD**	**Percent relative standard deviation**
IRAs	**Immediate Response Actions**	**SIM**	**Selective ion monitoring**
LCS	**Laboratory control sample**	**UCM**	**Unresolved complex mixture**
LLOQ	**Lower limit of quantitation**	**µg/m^3**	**micrograms per cubic meter**
MassDEP	**Massachusetts Department of Environmental Protection**	**VOCs**	**Volatile organic compounds**
MCP	**Massachusetts Contingency Plan**		

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

1.1 Overview of WSC-CAM-IX A

WSC-CAM-IX A, *Quality Control Requirements and Performance Standards for the Analysis of Air-Phase Petroleum Hydrocarbons (APH) by Gas Chromatography/Mass Spectrometry (GC/MS) in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*, is a component of MassDEP's Compendium of Analytical Methods (CAM). Effective October 15, 2024, this revised CAM protocol, WSC-CAM-IX A, replaces the previous version of the APH CAM document, WSC-CAM-IX A (effective date, July 1, 2010). 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 October 15, 2024 for the purpose of "Presumptive Certainty," the revised protocol may be used optionally prior to its effective date upon its publication on July 15, 2024.

This document provides Quality Control (QC) requirements and performance standards to be used in conjunction with MassDEP *Method for the Determination of Air-Phase Petroleum Hydrocarbons (APH)*, Revision 1 (December 2009). The QC requirements and performance standards specified in this document in Table IX A-2 together with the analytical procedures described in the MassDEP APH method, constitute the WSC-CAM-IX 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 APH method is a "Presumptive Certainty" requirement of WSC-CAM-IX A.

Sample preservation, container and analytical holding time specifications for air matrices for APH analyzed in support of MCP decision-making are presented in Appendix IX 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)*. Data reporting requirements are also provided in WSC-CAM-VII A. Reporting requirements specific to the air sampling protocol are provided in Section 3.2 of this CAM protocol.

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 or Lower Limits of Quantitation for WSC-CAM-IX A

The reporting limit (RL) or lower limit of quantitation (LLOQ) for an individual compound using WSC-CAM-IX 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 dilution factors, etc., as required. The CAM RLs/LLOQs for WSC-CAM-IX A target analytes and hydrocarbon ranges are:

- 2-5 µg/m^3 (0.1-0.5 parts per billion by volume [ppbV]) for APH target analytes; and
- 10-12 µg/m^3 for each hydrocarbon range.

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

RLs/LLOQs lower than the above-referenced CAM RLs/LLOQs for WSC-CAM IX A target analytes may be required to satisfy project requirements. The RL/LLOQ (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., MassDEP Indoor Air Threshold Values, background, etc.). Meeting MCP standards or criteria may require method modifications, such as the use of selective ion monitoring (SIM), an ion trap mass spectrometer, or other instrumentation of improved design to improve sensitivity. All such modifications must be described in the laboratory narrative. Regardless of the instrument or modification that is used, RLs/LLOQs for the WSC-CAM IX A 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-IX A

Each laboratory that uses the WSC-CAM-IX A protocol is required to operate a formal quality assurance (QA) 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) to assess analytical accuracy. Matrix duplicates (MD) may also be used to evaluate 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. These data must meet or exceed the performance standards as presented in Table IX A-2 of this protocol and the MassDEP APH Method. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in the MassDEP APH Method (Section 10.4). 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-IX A must include the following information:

QC Element	Performance Criteria
Bromofluorobenzene (BFB) Tuning	WSC-CAM-IX A, Table IX A-2
Initial Calibration	WSC-CAM-IX A, Table IX A-2
Continuing Calibration	WSC-CAM-IX A, Table IX A-2
Method Blanks	WSC-CAM-IX A, Table IX A-2
Average Recovery	MassDEP APH Method, Section 10.4
% Relative Standard Deviation (%RSD)	MassDEP APH Method, Section 10.4
Internal Standards	WSC-CAM-IX A, Table IX 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 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 IX 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-IX A protocol, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table IX A-2. It should be noted that the performance standards listed in Table IX 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/MS instrumentation as a quantitative tool and skilled in the interpretation of chromatograms and mass spectra.

1.2 Summary of MassDEP APH Method

This method is based on USEPA Method TO-15, *Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*.

Samples are collected in pre-cleaned, evacuated, passivated stainless steel canisters. A concentrator system is used for the automated collection, trapping, focusing, and injection of measured aliquots removed from the sample containers. Depending on the water retention properties of the packing, some or most of the water vapor contained in the sample completely passes through the concentrator during this process. Additional drying of the "trapped" sample aliquot, if required, is accomplished by forward purging the trap with clean, dry helium (or other inert gas).

Following preconcentration, the sample is transferred and cryogenically re-focused onto the inlet of a capillary column on a gas chromatograph (GC). The GC column is temperature-programmed to facilitate separation of the target analytes and hydrocarbon ranges of interest. All compounds are detected using a mass spectrometer that is interfaced directly to the GC. Target APH Analytes are identified and quantified using characteristic ions. Collective concentrations of C_9-C_{10} aromatic hydrocarbons are quantified using extracted ions. Collective concentrations of aliphatic hydrocarbon ranges are quantified using the total ion chromatogram. Identification of Target APH Analytes is accomplished by comparing sample electron impact mass spectra and retention times with the electron impact mass spectra and retention times of standards obtained under identical analytical conditions.

Average response factors (or calibration curves) determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of C_5 through C_8 and C_9 through C_{12} aliphatic hydrocarbons. An average response factor (or calibration curve) determined using an aromatic standard mixture is used to calculate a collective concentration of C_9 through C_{10} aromatic hydrocarbons. Response factors (or calibration curves) are also used to calculate individual concentrations of Target APH Analytes. The APH method marker compounds and retention time windows are summarized in Table IX A-1.

Table IX A-1: APH Method Range Marker Compounds		
Hydrocarbon Range	**Beginning Marker Compound**	**Ending Marker Compound**
C_5-C_8 Aliphatic Hydrocarbons	0.1 minutes before isopentane	0.01 minutes before n-nonane
C_9-C_{12} Aliphatic Hydrocarbons	0.01 minutes before n-nonane	0.1 minutes after dodecane
C_9-C_{10} Aromatic Hydrocarbons	0.1 minutes after o-xylene	0.1 minutes before naphthalene

1.3 Method Interferences

- Refer to the MassDEP APH Method 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 VOCs. After the analysis of a sample containing high concentrations of VOCs, one or more blanks should be analyzed to check for potential cross-contamination/carryover. Concentrations of VOCs which exceed the upper limit of calibration should prompt the analyst to check for potential cross-contamination/carryover.

- High methane and/or carbon dioxide levels may interfere with the chromatography. Dilution may be performed on samples to minimize this effect; however, the RLs/LLOQs for diluted samples will be proportionately increased. It should be noted that although the concentrator systems must be designed to minimize elevated levels of carbon dioxide, the potential still exists to have interfering levels.

- Certain organic compounds not associated with the release of petroleum products, including chlorinated solvents, ketones, and ethers may be detected by this method and may contribute to the collective response quantified within an aliphatic or aromatic hydrocarbon range. When requested by the data user, the identification of such non-APH compounds must be disclosed on the laboratory report form or laboratory narrative. See Table 7 of the MassDEP APH Method for a list of potential non-petroleum compounds which may contribute to hydrocarbon range concentrations.

1.4 Quality Control Requirements and Performance Standards for WSC-CAM-IX A

1.4.1 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/MS system may be found in Section 10 of the MassDEP APH Method.

1.4.2 Specific QC Requirements and Performance Standards for WSC-CAM-IX A

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

(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) 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*.

1.5 Special Analytical Considerations for WSC-CAM-IX A

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

- Petroleum products suitable for evaluation by this method include gasoline, as well as the volatile fractions of mineral spirits, kerosene, #2/diesel fuel oil, jet fuels, and certain petroleum naphthas. This method is not suitable for the identification and quantification of entrained aerosols, particulate-phase hydrocarbons, and petroleum products with a significant percentage of hydrocarbons with boiling points > 218°C.

  Compounds not meeting the regulatory definition of the aromatic and/or aliphatic fractions as defined in Sections 3.1.9, 3.1.10, and 3.1.11 of the APH 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. The concentration of a hydrocarbon range may be based on one (or just a few) peaks within the range and an indicative petroleum hydrocarbon peak pattern may not be apparent. Upon request by the data user, the laboratory may exclude these peaks that do not meet the regulatory definition. However, the laboratory must disclose the identification of the excluded peaks in the laboratory narrative.

NOTE: It is highly recommended that laboratories communicate the issue of potential non-petroleum hydrocarbons to the data user during the project set-up phase. Data users should be provided with the option for laboratories to visually review chromatograms, subsequently identify anomalous peaks inconsistent with a petroleum hydrocarbon signature, and exclude these peaks from the hydrocarbon range concentrations, if determined to be related to a non-petroleum hydrocarbon. Such practices will result in more accurate and more representative concentrations of the hydrocarbon ranges.

- The canister vacuum/pressure of all grab and time-integrated samples must be measured and documented upon receipt at the laboratory. An annually calibrated National Institute of Standards and Technology (NIST)-traceable vacuum/pressure gauge is attached to the canister inlet, the sampling valve is briefly opened and the vacuum/pressure is recorded. If the canister vacuum upon receipt at the laboratory is >15 inches of mercury (in. Hg) or if the canister vacuum measured upon receipt at the laboratory differs from the final canister vacuum measured in the field by more than ±5 in. Hg, the client should be contacted to determine if analysis should proceed. If client indicates that the analysis should proceed, the noted anomalies should be documented on the data report form or the laboratory narrative.

- It should be noted that laboratories may pressurize samples with ultra zero air or ultra-high purity nitrogen upon receipt. This may be performed as standard practice within the laboratory or only for samples which arrive at the laboratory with high vacuum levels (i.e., >15 in. Hg). If this is performed, the resulting dilution factor must be incorporated into the final result calculations. Pressurization should only be performed if samples contain high vacuum or if the RLs/LLOQs will not be adversely affected (i.e., above regulatory limits) as a result of the pressurization.

- 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 %RSD requirements specified in Table IX A-2.

Table IX A-2: Specific QC Requirements and Performance Standards for Air-Phase Petroleum Hydrocarbons (APH) Using WSC-CAM-IX 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 contain all target analytes. (3) Must follow procedure in Section 1.1.2 of this protocol and Section 10.4 of APH Method.	No	NA	Refer to Section 10.4 of the APH Method. See Section 1.1.2 of this protocol.	NA
GC Performance	Inter-laboratory Consistency and Comparability	n-Hexane and bromochloromethane (Internal Standard 1) must have a minimum separation of 50% (maximum peak height to valley height) in a 20 µg/m^3 calibration standard.	No	NA	Perform instrument/injection port maintenance as necessary.	Suspend all subsequent analyses until performance criteria are achieved. Report exceedances in the laboratory narrative.
GC/MS Tunes with BFB	Inter-laboratory Consistency and Comparability	(1) Criteria listed in Table 2 of APH Method. (2) Every 24 hours prior to sample analysis.	No	NA	Perform instrument maintenance as necessary; retune instrument.	Suspend all analyses until tuning non-compliance is rectified.
Initial Calibration	Laboratory Analytical Accuracy	(1) Must be analyzed at least once prior to analyzing samples, when 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 ≤RL/LLOQ. (4) %RSD ≤30 (except naphthalene ≤40), r ≥0.99 (linear regression), or r^2 ≥0.99 (non-linear regression) for each target analyte and hydrocarbon range. (5) If %RSD >30 (or 40 for naphthalene), linear or non-linear regression must be used. (6) Must contain all APH Components (see Table 1 of APH method) (7) Calibration must be performed under the same conditions as the samples. (8) Target analyte peaks in the calibration standard at the RL/LLOQ should be visually inspected to ensure peak signal	No	NA	(1) Recalibrate if target analytes or hydrocarbon ranges exceed %RSD, "r", or "r^2" criteria. (2) If recalculated concentrations from the lowest calibration standard are outside of 70-130% (or 60-140% for naphthalene) recovery range, either: * The RL/LLOQ must be reported as an estimated value[2], or * The RL/LLOQ must be raised to the concentration of the next highest calibration standard that exhibits acceptable recoveries when recalculated using the final calibration	Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds or hydrocarbon ranges (%RSD >30 [or 40 for naphthalene], 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 or hydrocarbon ranges affected.

Table IX A-2: Specific QC Requirements and Performance Standards for Air-Phase Petroleum Hydrocarbons (APH) Using WSC-CAM-IX 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
		distinguishable from background and to verify acceptable qualitative analyte identification (e.g., retention time and mass spectra). (9) If linear or non-linear regression used, verify the RL/LLOQ by recalculating concentrations in lowest calibration standard using the final calibration curve; recoveries must be 70-130% (except naphthalene 60-140%).			curve.	
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	Refer to LCS; ICV replaced with LCS.	No	NA	Refer to LCS; ICV replaced with LCS.	Refer to LCS; ICV replaced with LCS.
Continuing Calibration	Laboratory Analytical Accuracy	(1) Every 24 hours prior to the analysis of samples. (2) Concentration level near midpoint of curve. (3) Must contain all APH Components in Table 1 of APH Method. (4) Percent difference or percent drift (%D) must be ≤30 for each target analyte and hydrocarbon range.	No	NA	Recalibrate if %D for more than 1 compound or hydrocarbon range >30% or if any %D >50%.	Report non-conforming compounds or hydrocarbon ranges (%D >30) and associated samples in laboratory narrative. Note in the laboratory narrative if the %D indicates a low or high bias.
Method Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Every 24 hours prior to the analysis of samples. (2) Target analytes must be <RL/LLOQ except for C_{12} hydrocarbons and naphthalene which must be <2x the RL/LLOQ.	Yes	NA	If concentration of contaminant in sample is ≤10x concentration in blank, locate source of contamination; correct problem; reanalyze method blank and associated samples. 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

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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
						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.
Laboratory Control Sample (LCS)	Laboratory Analytical Accuracy	(1) Every 24 hours and after an initial calibration. (2) Concentration level near midpoint of curve. (3) Must contain all target analytes and representative hydrocarbon range compounds (see Section 9.4.12 of APH Method). (4) Must be obtained from a different source than that used to prepare the APH calibration standards. (5) Percent recoveries must be between 70-130% for target analytes and representative hydrocarbon range compounds except for naphthalene which must exhibit percent recoveries between 50-150%.	Yes	Recovery <10%; affects nondetect results for affected analyte in all samples analyzed under this LCS.	(1) If recoveries are low (<50% for naphthalene and <70% for remaining compounds), reanalyze LCS and associated samples. (2)If recoveries are high (>150% for naphthalene and >130% for remaining compounds), reanalyze LCS and associated samples if affected compounds were detected in associated samples; otherwise, re-analysis not required.	(1) If sample re-analysis is not possible, report non-conformance in laboratory narrative. (2) If recovery is outside of 70-130% (50-150% for naphthalene) for any analyte, report non-conforming compounds 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.
Matrix Duplicate (MD)	Method Precision in Sample Matrix	(1) Every 24 hours (sample selected at discretion of laboratory or at request of data user). (2) Relative percent differences (RPDs) ≤30 for results >5x the RL/LLOQ.	Yes ONLY when requested by the data user	NA	(1) If the RPD exceeds 30 and both results are >5x the RL/LLOQ, reanalyze the sample. (2) If an analyte is detected in one analysis at >5x the RL/LLOQ and not detected	Note exceedances in laboratory narrative.

Table IX A-2: Specific QC Requirements and Performance Standards for Air-Phase Petroleum Hydrocarbons (APH) Using WSC-CAM-IX 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
					in the duplicate analysis, repeat the analysis. (3) If an analyte is detected in one analysis at ≤5x the RL/LLOQ and not detected in the duplicate analysis, the RPD is not calculable and the analysis does not have to be repeated. (4) If an analyte is not detected in both the original and duplicate analyses, the RPD is not calculable. No further action is required.	
Internal Standards	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	(1) Minimum of 3 at retention times across GC run. Recommended internal standards are: Bromochloromethane 1,4-Difluorobenzene Chlorobenzene-d5 (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.	Yes	Recovery <20%; affects all nondetect results quantitated using affected internal standard in associated sample.	If one or more internal standards are outside of limits, re-analyze sample unless obvious interference present (e.g., unresolved complex mixture [UCM]). NOTE: If obvious interference is present and internal standard area would cause rejection of data (i.e., <20%), re-analyze sample on dilution.	(1) Report non-conformances in laboratory narrative. Include actual recovery of internal standard and provide summary of analytes quantitated using the internal standard. (2) If re-analysis yields similar internal standard non-conformances, the laboratory must report results of both analyses. (3) If re-analysis is performed within holding time and yields acceptable internal standard recoveries, the laboratory may report results of the re-analysis only. (4) If re-analysis is performed outside of the

Table IX A-2: Specific QC Requirements and Performance Standards for Air-Phase Petroleum Hydrocarbons (APH) Using WSC-CAM-IX 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
						holding time and yields acceptable internal standard 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) Quantitation must be based on internal standard calibration. (2) The laboratory must use the average response factor or linear or non-linear regression curve generated from the associated initial calibration for quantitation of each target analyte and hydrocarbon range. (3) The internal standard used for quantitation must be in accordance with Table 6 of the APH Method. (4) Results must be reported with 2 or more "significant figures" if ≥ RL/LLOQ. If reporting values below the RL/LLOQ, report with 1 or more "significant figures".[3]	NA	NA	NA	NA
Identification	NA	Refer to Section 9.5.2 of the APH Method.	NA	NA	NA	NA
Media Certification	Laboratory and Field Analytical Accuracy	(1) Batch or individual canister certification must be performed, as directed by the data user. (2) Canister certifications: target analytes or hydrocarbon ranges must be <½ the RL/LLOQ. (3) Flow controller calibration must be verified by the laboratory prior to sample collection and upon receipt with the samples. (4) RPD of the pre- and post-flow controller	Yes	NA	(1) Reclean canisters until certifications pass the acceptance criteria. Canisters must not be sent out for field sampling without an acceptable certification. (2) Narrate flow controller RPD non-conformances.	Report non-conformances in laboratory narrative.

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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
		calibration checks should be ≤20.				
General Reporting Issues	NA	(1) The laboratory must report values ≥ the sample-specific RL/LLOQ; optionally, values below the sample-specific RL/LLOQ can be reported as estimated, if requested. The laboratory must report results for samples and blanks in a consistent manner. (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> analyte. The associated QC (e.g., method blanks, LCSs) for each analysis must be reported. (3) Refer to Section 11.2 of the APH Method if non-APH compounds are requested by the data user. (4) Refer to Appendix IX A-1 for chain-of-custody (COC) requirements regarding preservation and holding times. (5) COC documentation requirements must be completed by the sampler as per Section 8.2.7 of the APH Method.	NA	NA	NA	(1) Qualification of the data is required if reporting values below the sample-specific RL/LLOQ. (2) Complete analytical documentation for diluted and undiluted analyses must be made available for review during an audit. (3) Non-APH compounds will be evaluated at the discretion of the data user consistent with the guidelines presented in Section 11.2 of the APH Method. (4) 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. (5) If canister vacuum on receipt is >15 in. Hg or if the laboratory receipt canister vacuum differs from final field vacuum by more than ±5 in Hg, the data user should be contacted before analysis can proceed; the canister vacuum anomalies must

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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
						be explained in the laboratory narrative. (6) If samples are analyzed outside of holding time, note the non-conformance in the laboratory narrative.

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

[2]If the RL/LLOQ is estimated due to unacceptable recovery of the lowest standard, the CAM RL/LLOQ 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.

[3]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.

1.6 Analyte List for WSC-CAM-IX A

The MCP analyte list for WSC-CAM-IX A is presented in Table IX A-3. The list is comprised of nine (9) target analytes and three (3) collectively quantified volatile hydrocarbon ranges.

It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL/LLOQ for the target analytes. Sources of various MassDEP standards and criteria include: Indoor Air Threshold Values and Sub-Slab Soil Gas Screening Values, MassDEP Vapor Intrusion Guidance: Site Assessment, Mitigation and Closure Policy # WSC-16-435, October 14, 2016.

1.6.1 Analyte List Reporting Requirements for WSC-CAM-IX A

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

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

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.

Table IX A-3: Analyte List for WSC-CAM-IX A (MassDEP APH)

Analyte	CASN
1,3-Butadiene	106990
Methyl-tert-butyl ether	1634044
Benzene	71432
Toluene	108883
Ethylbenzene	100414
m & p-Xylene[1]	1330207
o-Xylene[1]	95476
Naphthalene	91203
C_5-C_8 Aliphatic Hydrocarbons	NA
C_9-C_{12} Aliphatic Hydrocarbons	NA
C_9-C_{10} Aromatic Hydrocarbons	NA

CASN – Chemical Abstracts Service Number NA

– Not Applicable

[1]May be reported and evaluated as mixed isomers.

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-IX A

3.1 General Reporting Requirements for WSC-CAM-IX 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-IX A

Specific QC requirements and performance standards for WSC-CAM-IX A are presented in Table IX A-2. Specific reporting requirements for WSC-CAM-IX A are summarized below in Table IX A-4 as "Required Analytical Deliverables (**YES**)". 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.

Table IX A-4 Routine Reporting Requirements for WSC-CAM-IX A (MassDEP APH)

Parameter	Required Analytical Deliverable
GC Performance	***NO***
GC/MS Tunes	***NO***
Initial Calibration	***NO***
Initial Calibration Verification	***NO***
Continuing Calibration	***NO***
Method Blank	***YES***
Media Certification (canister and flow controller)	***YES***
Laboratory Control Samples (LCSs)	***YES***
Matrix Duplicate (MD)	***YES (if requested by data user)***
Internal Standards	***YES***
Non-APH Compounds	***YES (if requested by data user)***
Identification and Quantitation	***NO***
General Reporting Issues	***YES***
Other Air-Specific Reporting Requirements	
Pre-Sampling Information (Provided by Laboratory)	
Canister vacuum	***YES***
Canister serial number	***YES***
Flow controller serial number	***YES (if used)***
Date canister released from the laboratory	***YES***
Sampling Information (Provided By Sampler)	
Canister serial number for each sample identification	***YES***
Sampling duration	***YES (if time-integrated samples)***
Flow controller serial number for each sample identification	***YES (if used)***
Initial and final canister vacuums	***YES***
Post-Sampling Information (Provided by Laboratory)	
Vacuum of canister upon receipt at laboratory	***YES***
Flow controller calibration RPD	***YES (if used)***

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/LLOQ for each APH target analyte or hydrocarbon range must be adjusted (increased) in direct proportion to the Dilution Factor (DF).

The revised RL/LLOQ for the diluted sample, $RL/LLOQ_d$:

$$RL/LLOQ_d = DF \times \text{Lowest Calibration Standard for Target Analyte}$$

It should be understood that samples with elevated RLs/LLOQs as a result of a dilution may not be able to satisfy MCP standards/criteria in some cases if the $RL/LLOQ_d$ is greater than the applicable MCP standard or criterion to which the concentration is being compared. Such increases in RLs/LLOQs 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 50% of its associated highest calibration standard. This will avoid unnecessarily high RLs/LLOQs for other target analytes which did not require dilution.

NOTE: **DFs must also be taken into account if canisters are pressurized prior to analysis.** Refer to Section 9.5.1.3 of the MassDEP APH Method for dilution factor calculations under this scenario.

Appendix IX A-1

Sample Collection, Preservation, and Handling Procedures for Air-Phase Petroleum Hydrocarbon Analyses

Sample preservation, container and analytical holding time specifications for air matrices for APH 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	Holding Time[2,3]
Air	Certified clean, leak-free, stainless steel polished or silica lined passivated air sampling canisters	None	30 days

[1]The size of the canister will depend on project requirements.

[2]Holding time begins from time of sample collection.

[3]As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, 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.

Appendix IX A-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-IX A (MassDEP APH)	
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, correspondences
Miscellaneous Logs	Canister vacuum/pressure logs Injection logs Flow controller calibration logs
Initial Calibration Data	Summary of response factors for all standards in initial calibration; average response factors, %RSDs, correlation coefficients, and coefficients of determination for all target compounds and hydrocarbon ranges Chromatograms for all standards used in initial calibration Quantitation reports for all standards used in initial calibration Concentrations of standards used must be clearly presented
Continuing Calibration Data	Summary of %Ds and response factors Chromatograms for all continuing calibration standards Quantitation reports for all continuing calibration standards Concentrations of standards used must be clearly presented
Sample Results	Chromatograms for all sample analyses, re-analyses, and dilutions clearly demonstrating how hydrocarbon ranges, APH target analytes, and internal standards were integrated Quantitation reports for all sample analyses, re-analyses, and dilutions Mass spectra of reported positive results Summary of results, including RLs/LLOQs for each sample Date of analysis

DELIVERABLE REQUIREMENTS FOR DATA AUDITS WSC-CAM-IX A (APH)	
Method Blank Results	Chromatograms for all method blanks Quantitation reports for all method blanks Summary of results, including RLs/LLOQs Mass spectra of positive results in method blanks
LCS Results	Chromatograms for all LCSs Quantitation reports for all LCSs Summary of results, including concentrations detected, concentrations spiked, and percent recoveries
Matrix Duplicate Results (if performed)	Chromatograms for all matrix duplicates Quantitation reports for all matrix duplicates Summary of results, including original sample concentrations, matrix duplicate concentrations and RPDs
GC/MS Tune Data	BFB tune raw data: chromatogram, mass listing of BFB, and summary of tune results
QC Summaries	Internal standard performance
Other Information	Demonstration that LCS prepared from second source standard Chromatograms, quantitation reports and logs associated with canister certifications
Quantitation reports must exhibit area counts of target compounds and internal standards.	