State of Connecticut

Department of Energy and Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Gas Phase Aliphatic and Aromatic Hydrocarbons in Air and Soil Gas

by the

Massachusetts DEP APH Method

Version 3.0

Month 2023

Written by the Connecticut DEEP QA/QC Workgroup

Revision	Comments	Date
1.0	Draft version for public comment	November 2012
2.0	Final version	December 2014
3.0	Updates to reflect CAM method updates to improve consistency between different states.	Month 2023

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ACRONYNM LIST

ACRONYM	DEFINITION
APH	Air-phase petroleum hydrocarbons
BFB	Bromofluorobenzene
CASN	Chemical Abstracts Service Number
CCV	Continuing calibration verification
%D	Percent difference or percent drift
DF	Dilution factor
EP	Environmental professional
GC	Gas chromatograph
GC/MS	Gas chromatography/mass spectrometry
ICV	Initial calibration verification
In. Hg	Inches of mercury
LCS	Laboratory control sample
LCSD	Laboratory control sample duplicate
LLOQ	Lower Limit of Quantitation
MassDEP	Massachusetts Department of Environmental Protection
MD	Matrix duplicate
NA	Not applicable
ppbV	Parts per billion (volume)
QA	Quality assurance
QC	Quality control
%R	Percent recovery
%RSD	Percent relative standard deviation
r/r^2	Correlation coefficient
RCP	Reasonable Confidence Protocols
RL	Reporting limit
RPD	Relative percent difference
RSR/RSRs	Remediation Standard Regulations
SIM	Selective ion monitoring
UCM	Unresolved complex mixture
$\mu g/m^3$	micrograms per cubic meter
VOCs	Volatile organic compounds

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1.0 Quality Assurance and Quality Control Requirements for MassDEP APH Method

1.1 Method Overview

The Air Petroleum Hydrocarbons ("APH") Method ("the APH Method") is designed to measure the gaseous-phase concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in air and soil gas. Volatile aliphatic hydrocarbons are collectively quantified within two carbon number ranges: C_5 through C_8 and C_9 through C_{12}. Volatile aromatic hydrocarbons are collectively quantified within the C_9 to C_{10} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 28°C (isopentane) and 218°C (naphthalene). This method may also be used to identify and quantify specific Target Analytes, including BTEX analytes.

All references to SW-846 Methods (i.e., SW-846 8000, 8260, etc.) in this document refer to the United States Environmental Protection Agency's most recently published version. All references to "the VPH Method" in this document refer to latest promulgated version of the Massachusetts DEP VPH Method.

The APH Method is designed to complement and support the toxicological approach developed by the Connecticut Department of Energy and Environmental Protection ("DEEP") to evaluate human health hazards that may result from exposure to air-phase hydrocarbons. It is intended to produce data in a format suitable for evaluation by that approach.

Overall usability of data produced using this RCP protocol should be evaluated for compliance with project-specific data quality objectives, regardless of "Presumptive Certainty" status.

1.2 Summary of the 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 refocused onto the inlet of a capillary column in a gas chromatograph ("GC"). The GC oven is temperature-programmed to facilitate separation of the target analytes and hydrocarbon ranges of interest. All compounds are detected using a mass spectrometer ("MS") that is interfaced directly to the GC. Target APH Analytes are identified and quantified using characteristic ions. Identification of target analytes is accomplished by comparing sample electron impact mass spectra with the electron impact mass spectra of standards obtained under identical analytical conditions. 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.

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 APH target analytes. APH method range marker compounds can be found in the APH method.

1.3 Method Interferences

1.3.1 Chemical Contaminants

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 levels and/or carbon dioxide levels may interfere with the chromatography. Dilution may be performed on samples to minimize this effect; however, the reporting limits/lower limits of quantitation ("RL/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 MassDEP APH Method for a list of potential non-petroleum compounds which may contribute to hydrocarbon range concentrations.

1.4 Quality Control Requirements for the APH Method

1.4.1 Reporting Limits/Lower Limits of Quantitation for APH Method

The reporting limit ("RL"), or lower limit of quantitation ('LLOQ") for an individual compound 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. Table 1.0 lists approximate RL/LLOQs for air utilizing GC/MS.

Table 1.0: Typical Reporting Limits/Lower Limits of Quantitation

Analyte	Typical Reporting Limit
1,3-Butadiene	2-5 µg/m^3/ 0.1-0.5 ppbV
Methyl-tert-butyl ether	2-5 µg/m^3/ 0.1-0.5 ppbV
Benzene	2-5 µg/m^3 / 0.1-0.5 ppbV

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Analyte	Typical Reporting Limit
Toluene	2-5 µg/m^3/ 0.1-0.5 ppbV
Ethylbenzene	2-5 µg/m^3/ 0.1-0.5 ppbV
m & p-Xylene	2-5 µg/m^3/ 0.1-0.5 ppbV
o-Xylene	2-5 µg/m^3/ 0.1-0.5 ppbV
Naphthalene	2-5 µg/m^3/ 0.1-0.5 ppbV
C_5-C_8 Aliphatic Hydrocarbons	10-12 µg/m^3
C_9-C_{12} Aliphatic Hydrocarbons	10-12 µg/m^3
C_9-C_{10} Aromatic Hydrocarbons	10-12 µg/m^3

Sample dilution or lower sample volume will also cause the RLs/LLOQs to be raised. 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 to meet Remediation Standard Regulation ("RSR") criteria. To meet the detection limits it may be necessary to modify the analytical method by using increased sample volume or mass or employing selective ion monitoring. In such cases, the modifications must be noted in the laboratory report narrative.

1.4.2 General Quality Control Requirements

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 for volatile organics. Each analyst must demonstrate the ability to produce acceptable quantitative and qualitative results both for individual target analytes and aliphatic hydrocarbon ranges with this method.

Refer to SW-846 Method 8000 for general quality control ("QC") requirements for all chromatographic methods, including the APH Method. These requirements ensure that each laboratory maintain a formal quality assurance ("QA") program and records to document the quality of all chromatographic data and be certified by the Connecticut Department of Public Health for the analysis performed. QC procedures necessary to evaluate the GC /MS system operation may be found in SW-846 Method 8000 and include evaluation of calibrations and chromatographic performance of sample analyses. Instrument QC and method performance requirements for the GC/MS system may be found in the APH Method.

The minimum requirements for a formal QA program include an Initial Demonstration of Capability ("IDOC"), ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples ("LCS") to assess accuracy and matrix duplicates ("MD") to assess precision. Percent recovery data from site-specific samples allow the environmental professional ("EP") to make informed decisions regarding contamination levels at the site. Batch MD results do not give any indication of site-specific matrix interferences or analytical problems related to the specific site matrices and are in general discouraged. Blanks should not be used for MDs.

Laboratories must document and have on file an IDOC for each combination of sample preparation and determinative method being used. These data must meet, or fall within, the performance standards as presented in Section 1.4 and Table 1A of this RCP. An IDOC must be completed and documented when a method is initially started up, whenever a method is substantially modified, or new laboratory staff is trained to perform the APH Method. The IDOC must include the following elements provided in Table 2.0:

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Table 2.0: IDOC Requirements

QC Element	Performance Criteria
4-Bromofluorobenzene (BFB) Tuning	APH Method
Initial Calibration	Table 1A
Continuing Calibration	Table 1A
Method Blanks	Table 1A
Matrix Duplicate	Table 1A
Laboratory Control Samples	Table 1A
Average Recovery	APH Method
% Relative Standard Deviation	APH Method
Internal Standards	Table 1A

Laboratories are required to generate laboratory specific performance criteria for LCS compound recovery limits, and relative percent difference (“RPD”) limits, and surrogate recovery limits. These limits must be equal to or fall within the limits specified in Table 1A.

1.4.3 Specific QA/QC Requirements and Performance Standards for the APH Method

Specific QA/QC requirements and performance standards for the APH Method are presented in Table 1A. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide the environmental professional with “Reasonable Confidence” regarding the usability of analytical data to support environmental decisions. The concept of "Reasonable Confidence" is explained on the DEEP website.

While optional, parties electing to utilize these protocols will be assured that agency reviewers will, generally, accept "Reasonable Confidence" data. To achieve “Reasonable Confidence” parties must:

1. Comply with the applicable QC analytical requirements prescribed in Table 1A for this test procedure;

2. Evaluate and narrate all protocol non-compliances and implement, as necessary, required corrective actions and analytical response actions for all non-conforming analytical performance standards; and

3. Retain reported and unreported analytical data and information for a period of 10 years.

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Table 1A: Specific QA/QC Requirements and Performance Standards for RCP APH Method

Required QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	Required Corrective Action Column 5	Analytical Response Action Column 6	Rationale – (this column will be removed from the final version)
Initial Demonstration of Capability ("IDOC")	Laboratory Analytical Accuracy & Precision	(1) Must be performed prior to using method on samples. (2) Must be performed for each matrix. (3) Must contain all target analytes. (4) Must follow procedure in SW-846 8000.	No	Refer to SW-846 8000 and Section 1.4.2 of this protocol.	NA	Removed specific section references.
GC Performance	Inter-laboratory Consistency and Comparability	(1) n-Hexane and bromochloromethane (IS1) must have a minimum separation of 50% (maximum peak height to valley height) in a 20 µg/m^3 calibration standard.	No	Perform instrument/injection port maintenance as necessary.	Suspend all subsequent analyses until performance criteria are achieved. Report exceedances in the laboratory narrative.	Group accepted MA language
GC/MS Tunes with BFB	Inter-laboratory Consistency & Comparability	(1) Criteria listed in APH Method. (2) Every 24 hours prior to sample analysis.	No	Perform instrument maintenance as necessary; retune instrument.	Suspend all analyses until tuning non-compliance is rectified.	Group accepted MA language
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 ≤RL/LLOQ. (4) %RSD ≤30 (except for naphthalene ≤40), r >0.99 (linear regression), or r^2 >0.99 (non-linear regression) for each target analyte. (5) If %RSD >30 (or 40 for	No	(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[1], or *The RL/LLOQ must be raised to the concentration	Sample analysis cannot proceed without a valid initial calibration. Report non-conforming compounds (%RSD >30 [or 40 for naphthalene], r <0.99, r^2 <0.99) in laboratory report narrative. If non-linear regression (i.e., quadratic equation) is used for calibration, this must be noted in the	Group accepted MA language

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Required QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	Required Corrective Action Column 5	Analytical Response Action Column 6	Rationale – (this column will be removed from the final version)
		naphthalene), linear or non-linear regression must be used. (6) Must contain all APH components (see APH Method). (7) Calibration must be performed under the same conditions as the samples. (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%).		of the next highest calibration standard that exhibits acceptable recoveries when recalculated using the final calibration curve.	laboratory report narrative along with the compounds affected.	
Initial Calibration Verification ("ICV")	Laboratory Analytical Accuracy	(1) Immediately after each initial calibration. (2) Concentration level near midpoint of curve. (3) Prepared using standard source different than used for initial calibration. (4) Must contain all target analytes. (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%. (6) An LCS can be analyzed in lieu of an ICV, see LCS below.	No	(1) Compounds must recover within 70-130% (2) Laboratories are allowed to have 20% of compounds out, as long as all compounds within recover 40 -160%. (3) Locate source of problem; recalibrate if >10% of all analytes are outside of criteria.	If recovery is outside of 70-130% for any analyte (or 60-140% for naphthalene), report non-conforming compounds in laboratory report narrative.	Group used language from other RCPs to maintain consistency between all RCP docs, added Item 6 in Column 3 from MA.

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Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Analytical Response Action** Column 6	**Rationale – (this column will be removed from the final version)**
Continuing Calibration Verification ("CCV")	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 APH Method. (4) %D must be ≤30 for each target analyte.	No	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.	Group used 8260 language adjusted for APH method.
Method Blank ("MB")	Laboratory Method Sensitivity (contamination evaluation)	(1) Every 24 hours prior to analysis of samples. (2) Target analytes must be ≤½ RL/LLOQ except C_{12} hydrocarbons and naphthalene which must be <2x the RL/LLOQ.	Yes	(1) If concentration of contaminant in sample is <10x concentration in blank, locate source of contamination; correct problem; reanalyze 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 reanalysis is not possible, report non- conformance in laboratory report 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 report narrative. (3) If reanalysis is performed within holding time and yields	Group used similar language as other RCPs

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Required QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	Required Corrective Action Column 5	Analytical Response Action Column 6	Rationale – (this column will be removed from the final version)
					acceptable method blank results, only report results of the reanalysis. (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) Prepared using standard source different than used for initial calibration. (4) Must contain all target analytes and representative hydrocarbon range compounds (see APH Method). (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	(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, reanalysis 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.	Group used similar language as RCPs, but adjusted recoveries to match MA language

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Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Analytical Response Action** Column 6	**Rationale – (this column will be removed from the final version)**
Matrix Duplicate ("MD")	Method Precision in Sample Matrix	(1) Every 24 hours (sample selected at discretion of laboratory or at request of data user).	Yes ONLY when requested by the data user	(1) If the RPD exceeds 30 and both results are >5x the RL/LLOQ, reanalyze the sample.	Note non-conformances in laboratory narrative.	Group accepted MA language
Internal Standards	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	(1) Minimum of 3 at retention times across GC/MS run. Recommended internal standards are: • Bromochlorodemethane • 1,4-Difluorobenzene • Chlorobenzene- (2) Area counts in samples must be between 50 – 200% of the area counts in the associated continuing calibration standard. (3) Retention times of internal standards must be within ±30 seconds of retention times in associated continuing calibration standard.	No	If one or more internal standards are outside of limits, reanalyze sample unless obvious interference present (e.g., UCM). NOTE: If obvious interference is present and internal standard area would cause rejection of data (i.e., <20%), reanalyze sample on dilution.	(1) Report non-conformances in laboratory report narrative. Include actual recovery of internal standard and provide summary of analytes quantitated using the internal standard. (2) If reanalysis yields similar internal standard non-conformances, the laboratory must report results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable internal standard recoveries, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of the holding time and yields acceptable internal standard recoveries, the laboratory must report results of both analyses.	Group accepted MA language

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Required QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	Required Corrective Action Column 5	Analytical Response Action Column 6	Rationale – (this column will be removed from the final version)
					(5) If sample is not reanalyzed 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 analyte. (3) The internal standard used for quantitation must be in accordance with the APH Method.	NA	NA	N/A	Group used similar language from other RCPs
Identification	NA	Refer to the APH Method	NA	NA	NA	Group accepted MA language
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 calibration checks should be <20.	Yes	(1) Reclean canisters until certifications pass the acceptance criteria. (2) Canisters must not be sent out for field sampling without an acceptable	Report non-conformances in laboratory narrative.	Group accepted MA language

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Required QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**Required Corrective Action** Column 5	**Analytical Response Action** Column 6	**Rationale – (this column will be removed from the final version)**
General Reporting Issues	NA	(1) Do not report concentrations below the RL/LLOQ. Concentrations below the RL/LLOQ are reported as "ND" with the RL/LLOQ. If reporting estimated concentrations below the RL/LLOQ, labs must indicate that RCP was not followed. (2) The full analyte list in Table 1B must be reported in order to obtain Reasonable Confidence. (3) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, LCSs, etc.) for each analysis must be reported. (4) Refer to the APH Method if non-APH compounds are requested by the data user.	NA		(1) Complete analytical documentation for analyses must be made available for review upon request. (2) Non-APH compounds will be evaluated at the discretion of the data user consistent with the guidelines presented in the APH Method. (3) The performance of dilutions must be documented in the laboratory report narrative or on the report form. Unless due to elevated concentrations of target compounds, reasons for dilutions must be explained in the laboratory report narrative. (4) 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 pressure anomalies must be	Group used similar language from other RCPs. Column 6, item 4: group accepted MA language.

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Required QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	Required Corrective Action Column 5	Analytical Response Action Column 6	Rationale – (this column will be removed from the final version)
					explained in the laboratory narrative. (5) If samples are analyzed outside of the holding time, note the non-conformances in the laboratory report narrative.	
If the RL/LLOQ is estimated due to unacceptable recovery of the lowest standard, the RL/LLOQ has not been achieved; Question 5b of the "Reasonable Confidence Protocol Laboratory Analysis QA/QC Certification Form" must be answered "NO" and this must be addressed in the laboratory report narrative.						

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1.5 Special Analytical Considerations for the APH Method

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 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.

The canister pressure of all grab and time-integrated samples must be measured and documented upon receipt at the laboratory. An annually calibrated NIST-traceable vacuum/pressure gauge is attached to the canister inlet, the sampling valve is briefly opened, and the pressure is recorded. If the canister vacuum on receipt is >15 inches of mercury (in. Hg) or if the canister vacuum measured on 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 reporting limits 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 percent relative standard deviation ("%RSD") requirements specified in Table 1A.

1.6 Analyte List for MassDEP APH Method

The DEEP analyte list for the APH Method is presented in Table 1B. The compounds listed are readily analyzable by the APH Method.

Table 1B: Analyte List for the APH Method

Analyte	CAS No.
1,3-Butadiene	106990
Methyl-tert-butyl ether	1634044
Benzene	71432
Toluene	108883

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Analyte	CAS No.
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
[1]May be reported and evaluated as mixed isomers	

1.6.1 Additional Reporting Requirements for the APH Method

While it is not necessary to request and report all the APH analytes listed in Table 1B to obtain Reasonable Confidence status, it is necessary to document such a limitation, for site characterization and data representativeness considerations. DEEP strongly recommends that the full list of analytes be reported during the initial stages of a site investigation and/or at sites with an unknown or complicated history of chemical usage or storage.

In cases where a shortened list of analytes is selected, the laboratory must still meet the method specific quality control requirements and performance standards associated with the requested analytes list to obtain Reasonable Confidence.

1.7 Routine Reporting Deliverables for MassDEP APH Method

The following table (Table 3.0) lists the routine report deliverables. Note that while laboratories are not required to report certain items, they must keep the data on file and may be required to report these items in special circumstances.

Table 3.0: Report Deliverables

Parameter	Deliverable	Comments
GC Performance	NO	Analysis cannot proceed without meeting tuning criteria.
GC/MS Tunes	NO	Analysis cannot proceed without meeting tuning criteria.
Initial Calibration	NO	Note non-conformances in laboratory report narrative
Initial Calibration Verification	NO	Note non-conformances in laboratory report narrative
Continuing Calibration Verification	NO	Note non-conformances in laboratory report narrative
Method Blanks	YES	Note non-conformances in laboratory report narrative. Flag all positive results above RL/LLOQ with “B” flag.
Media Certification (canister & flow controller)	YES	
Lab Control Sample/Lab Control Sample Duplicate	YES	Note non-conformances in laboratory report narrative
Matrix Duplicate	YES	Note non-conformances in

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Parameter	Deliverable	Comments
	(If requested)	laboratory report narrative
Internal Standards	YES	Note non-conformances in laboratory report narrative
Tentatively Identified Compounds Non-APH Compounds	YES (If requested)	Flag all concentrations as estimated ("J" Flag)
Identification and Quantitation	NO	Note non-conformances in laboratory report narrative
General Reporting Issues	YES	Note non-conformances in laboratory report narrative
QA/QC Certification Form	YES	Signed by laboratory director or their designee
Chain-of-Custody Form	YES	Signed by sample collector, courier, and laboratory.
Pre-Sampling Information (Provided by Laboratory)		
Canister vacuum	YES	Note information in report for each sample.
Canister serial number	YES	Note information in report for each sample.
Flow controller serial number	YES (if used)	Note information in report for each sample.
Date canister released from the laboratory	YES	Note information in report for each sample.
Sampling Information (Provided By Sampler)		
Canister serial number for each sample identification	YES	Note information in report for each sample.
Sampling duration	YES (if time-integrated samples)	Note information in report for each sample.
Flow controller serial number for each sample identification	YES (if used)	Note information in report for each sample.
Initial and final canister vacuums	YES	Note information in report for each sample.
Post-Sampling Information (Provided by Laboratory)		
Vacuum of canister upon receipt at laboratory	YES	Note information in report for each sample.
Flow controller calibration RPD	YES (if used)	Note information in report for each sample.

1.7.1 Reporting and Flagging of Results

The following rules apply to reporting results:

- Non-Detects: Report all non-detects and results below the reporting limit as "ND" (Not Detected at the Specified RL/LLOQ). The RL/LLOQ for each compound in each sample must be listed on the report, based upon the lowest calibration standard, the exact sample mass, any dilution factors, percent moisture, etc.

- Compounds detected above the RL/LLOQ in blanks and in samples shall be flagged with a "B" suffix (e.g., 25B).
- Report results for any library search compounds as estimated using a "J" suffix (e.g., 25J).

1.8 Sample Collection, Storage and Holding Times

Table 4.0 identifies the type of containers, storage requirements, and holding times.

Table 4.0: Sample Containers, Storage and Holding Times

Matrix	Container[1]	Storage	Holding Time[2]
Air	Certified clean, leak-free, stainless steel polished or silica lined passivated air sampling canisters. Cannister pressure must be >15 in. Hg upon receipt.		30 days

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

[2]Holding time begins from time of sample collection. If the holding time is exceeded by >2x the allowable holding time, data users should consider non-detect results as unusable and positive results as estimated with a significantly low bias.